Significance and Treatment of Dissolved Solids in Wastewaters from Canadian Steam Electric Stations

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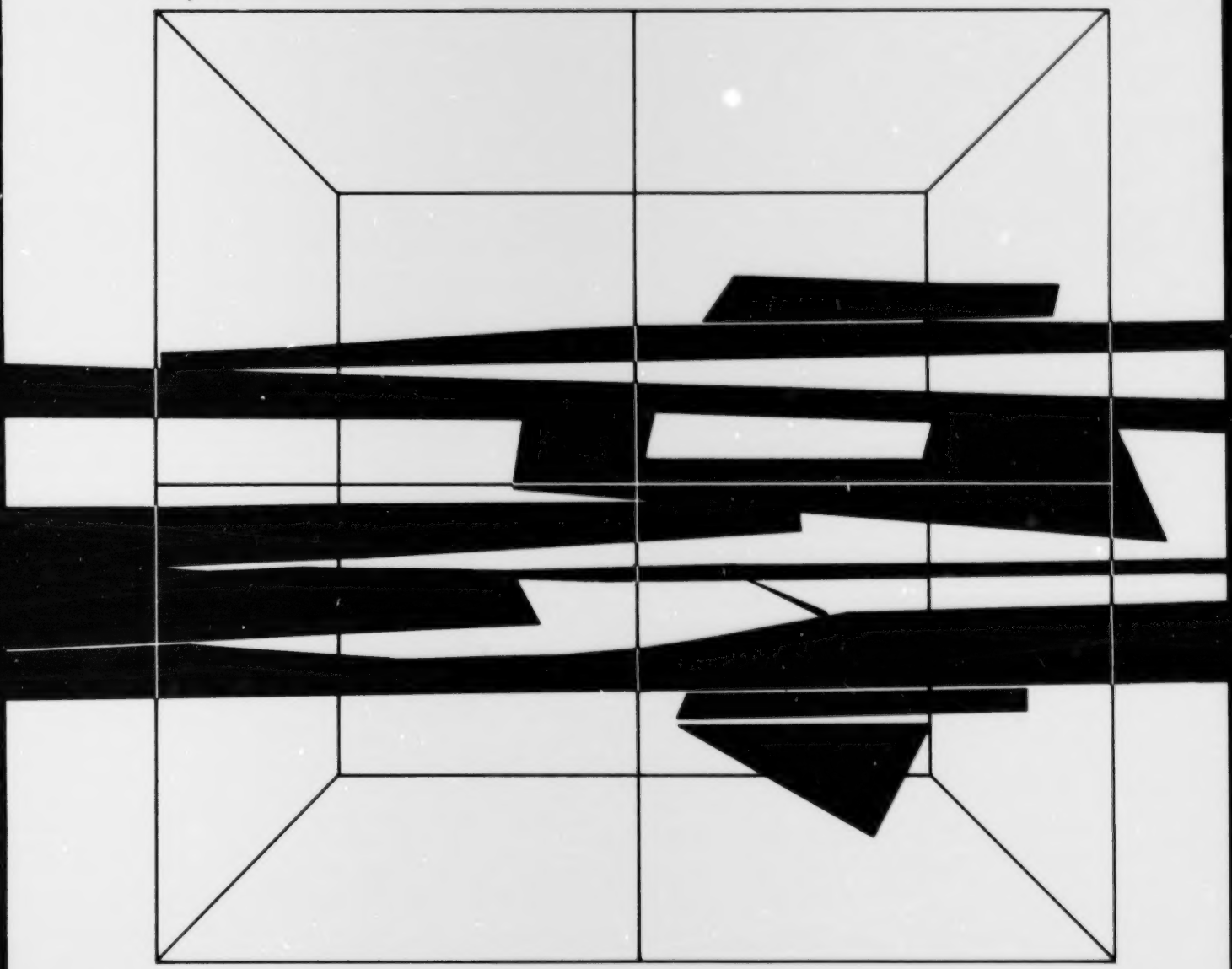

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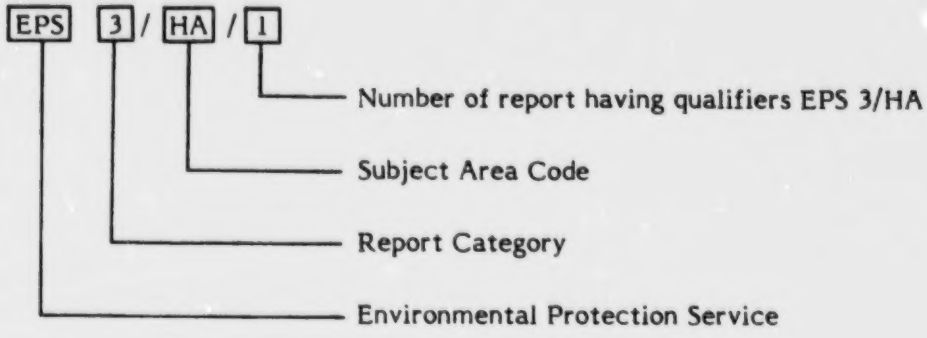

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SIGNIFICANCE AND TREATMENT OF DISSOLVED SOLIDS IN WASTEWATERS FROM CANADIAN STEAM ELECTRIC STATIONS

by

Dearborn Environmental Consulting Services

for the

Industrial Programs Branch
Environmental Protection Service
Environment Canada

EPS 3/PG/3
May 1986

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Cat. No. En 49-9/3-3E
ISBN 0-662-14656-5
BEAUREGARD PRESS LIMITED

ABSTRACT

Natural surface waters (streams, lakes, rivers) contain a variety of chemicals in solution. Many different dissolved substances are normally present in trace amounts but the same relatively few substances invariably make up the bulk of the total dissolved constituents.

Changes in the proportions of the major constituents and/or their total concentration may adversely affect aquatic organisms. Levels of tolerance to such changes vary considerably from organism to organism. There is a paucity of information on the analytical methods used and changes in individual ion concentrations in the scientific literature; therefore, it is often unclear whether compositional or overall concentration changes have been responsible for the observed effects.

Several common measurements of the overall dissolved substance concentration, known as the total dissolved substance or "TDS" concentration, are based on the assumption that the bulk of the TDS is composed of the same relatively few major dissolved constituents. Although this may be true for many natural surface waters, it cannot be assumed that "safe" TDS levels in natural surface waters indicate that comparable TDS levels in industrial wastewaters are also environmentally safe. TDS analysis methods for natural waters may also produce significantly inaccurate TDS measurements of certain industrial wastewaters.

TDS levels in wastewaters produced by the coal-fuelled steam electric power generation industry are often significantly higher than those normally encountered in natural surface waters. Their major TDS constituent makeup ranges from compositions which are similar to those in natural surface waters through compositions in which there is a significant imbalance in the major natural TDS constituents, to those where normally "trace" metallic and "abnormal" constituents contribute significantly to the TDS concentration. A variety of methods for the reduction of TDS levels in such wastewaters are either demonstrated practicable technology or are under development. These methods are increasingly important with increasing emphasis on water quality.

RÉSUMÉ

Les eaux naturelles de surface (lacs et cours d'eau) renferment diverses matières chimiques en dissolution, certaines s'y trouvant normalement en traces, quelques-unes, à peu près toujours les mêmes, composant le gros des constituants dissous.

Les organismes aquatiques peuvent souffrir des modifications de la proportion ou de la concentration totale des principaux constituants. La tolérance varie considérablement d'un organisme à l'autre. Les publications scientifiques renseignent peu sur les méthodes d'analyse et sur les modifications de concentration de chaque ion; souvent, il est donc difficile d'attribuer les effets observés à des modifications soit de la composition, soit de la concentration.

Les dosages habituels des matières totales en dissolution (MTD) reposent souvent sur l'hypothèse que ces matières réunissent, en gros, les mêmes constituants relativement peu nombreux. Cela peut être vrai dans beaucoup d'eaux de surface, mais on ne peut pas supposer que les concentrations inoffensives de MTD dans les eaux de surface le seront dans les eaux résiduaires industrielles. Les méthodes d'analyse des MTD des eaux naturelles peuvent se révéler notablement inexactes quand il s'agit de doser certains effluents industriels.

Les concentrations de MTD dans les effluents des centrales électriques à charbon sont souvent plus fortes que celles qu'on observe normalement dans eaux naturelles de surface. La composition de ces effluents, en ce qui concerne les principaux constituants en dissolution, peut ressembler à celle des eaux naturelles ou s'en écarter au point qu'on y trouve des concentrations relativement élevées de métaux normalement en traces ou exceptionnels. Diverses techniques practicables d'épuration ont été éprouvées ou elles sont en cours de perfectionnement. Elles prennent de plus en plus d'importance, eu égard à la prééminence qu'on accorde à la qualité de l'eau.

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ACKNOWLEDGEMENTS

This study was conducted by R. Kissel of Dearborn Environmental Consulting Services. Mr. L.A. Dwyer was project manager and scientific authority and S. Wheatley was technical editor and production supervisor for the Environmental Protection Service.

1 INTRODUCTION

The quality of water in relation to a particular use often involves a consideration of the kinds and quantities of chemical impurities it contains. The sum of these impurities known as the "total solids content" is normally divided into the total dissolved solids (TDS) and total suspended solids (TSS) fractions.

In natural surface waters, the total solids content is influenced chiefly by the characteristics of the soil and rocks forming the drainage basin or aquifer, and the length of time the water is in contact with them. Theoretically, many dissolved chemicals can be components of the total dissolved solids content. For most natural waters, however, the bulk of the total dissolved solids (TDS) content is made up of the same, few ions. As a result, the TDS content in natural waters is commonly calculated from the concentrations or assumed concentrations of only a few major ions including sodium, the "hardness" ions (calcium and magnesium), and the commonly associated ions carbonate, chloride, and sulphate.

The regional distribution of the total dissolved solids (based on the major ion content) of surface waters across Canada is shown in Figure 1. The total of these ions varies considerably in each region. Although most surface waters in Canada have a total concentration of less than 150 mg/L, values for the southern prairie region are particularly high with TDS concentrations in excess of 300 mg/L.

Streams in regions of low runoff generally contain greater TDS concentrations than streams in regions of high runoff. Subsurface waters in all regions usually contain more dissolved solids than surface waters and TDS levels may fluctuate considerably with seasonal change.

Figure 2 shows the average annual concentrations of calcium, magnesium, sodium, bicarbonate, sulphate and chloride in Canadian surface waters. The concentrations of these ions vary depending on surface geology and regional climatic patterns. One example of this is observed in sedimentary formations where calcium is present in calcite, dolomite and sandstone. These formations have high rates of dissolution and produce higher concentrations of calcium (up to several hundred mg/L) in water passing over them. Sodium is found in all surface waters and may range in concentrations from several milligrams per litre in dilute stream runoff areas to several thousand milligrams per litre in brines of closed basins. In comparison, seawater contains between 3.3 and 3.6 percent (33 000 to 36 000 mg/L) dissolved solids.

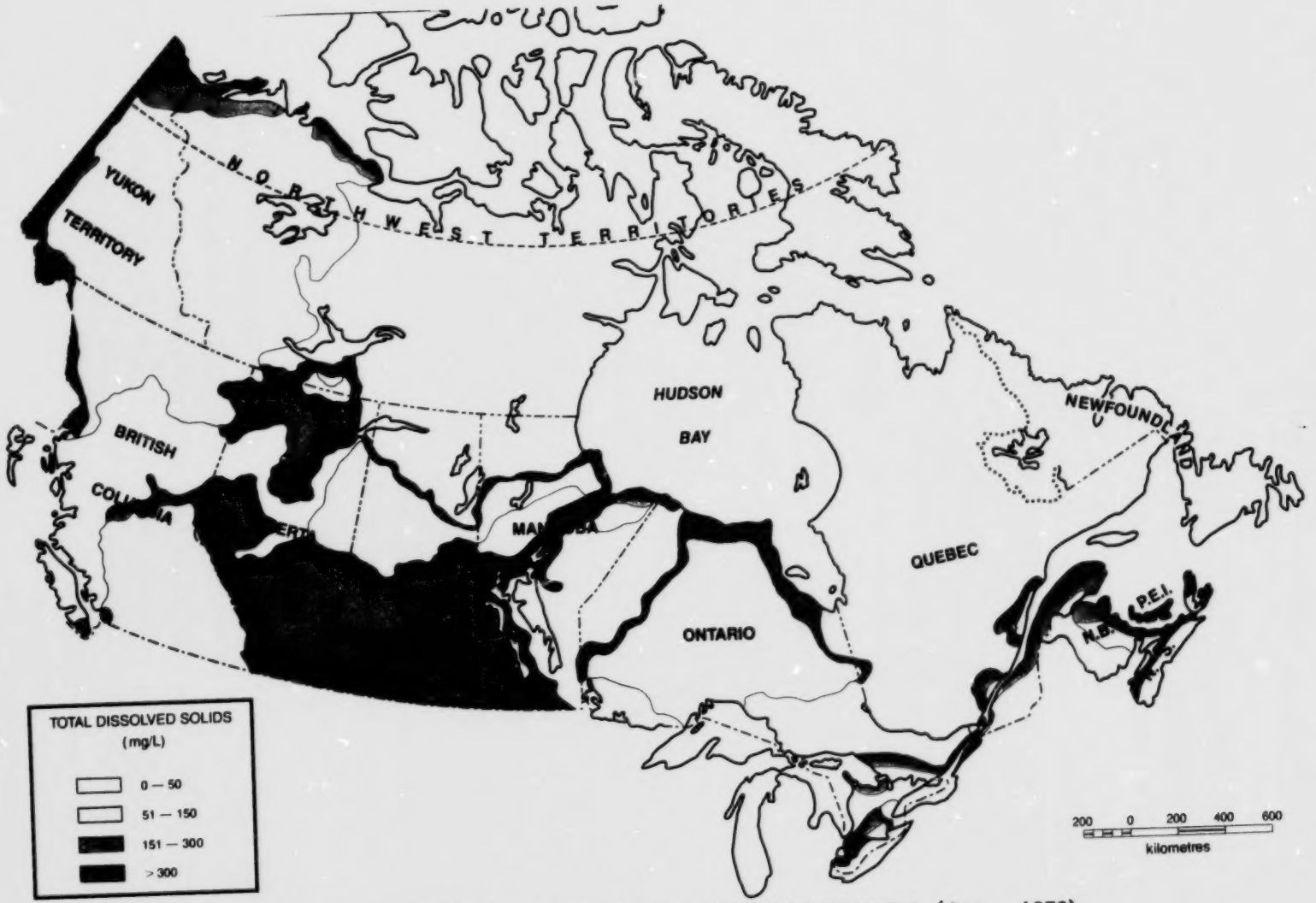


FIGURE 1 TOTAL DISSOLVED SOLIDS OF SURFACE WATERS IN CANADA (Anon., 1978)

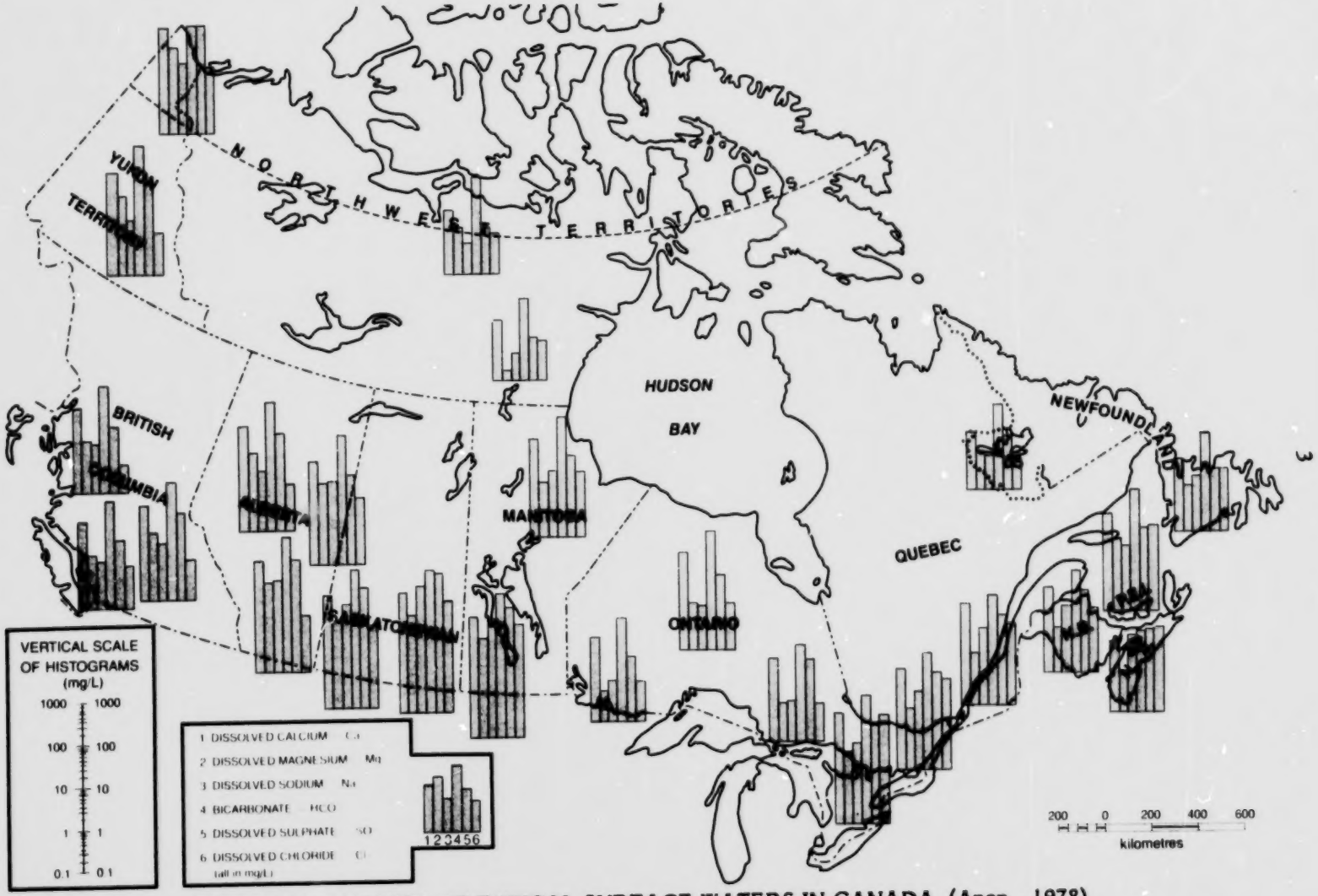


FIGURE 2 CHEMICAL QUALITY OF TYPICAL SURFACE WATERS IN CANADA (Anon., 1978)

The changes in the TDS of water as it passes through the hydrologic cycle from rainfall to the sea are summarized in Figure 3. Rainwater which contains very few dissolved solids becomes ten thousand times more saline by the time it enters the sea. A one hundred thousand times increase exceeds saturation, and can occur in natural salt pans.

In contrast to natural waters, industrial wastewaters cannot be relied upon to be composed primarily of the same common ions or to have comparable TDS concentrations. During use, industrial waters may become contaminated with a variety of substances which are not normally present or are only present in very small, safe amounts in surface waters. Industrial processes such as cooling which tend to evaporate some portions of the process water often result in a concentration of dissolved solids in the remaining water. For this reason, the dissolved solids contents of industrial wastewaters may present problems when environmentally safe discharges, subsequent industrial uses which require high purity water, or wastewater disposal are contemplated.

One of the major industrial users of Canadian surface waters is the steam electric power generation industry. The majority of the water intake requirement for steam electric stations is used for main condenser cooling. Water is also used to cool auxiliary equipment, provide make-up water to the boilers for steam, clean boilers and furnaces and, particularly in coal-fuelled stations, remove and transport combustion wastes.

In older power station designs, water was used in copious amounts and almost exclusively on a once-through basis for each separate subsystem. However, with the increasing competition for the use of clean surface water supplies by industries, agriculture and the public, the traditional once-through water use patterns in many industries including the steam electric industry, have been changing rapidly. The emphasis in new designs is on reduced water intake, maximum internal re-use of service water streams through recirculation, and reduction of wastewater volumes to be treated in order to facilitate removal of maximum amounts of contaminants before discharge. In some of the newest North American power stations, water system designs and management practices have been developed to achieve essentially zero discharge. This development has resulted in problems for the power generation industry. The continued reuse of service waters within a station results in dissolved and suspended solids concentrations which are considerably greater than what the older service water systems were designed to accommodate. While increased concentrations of potentially toxic substances in reduced wastewater volumes is desirable for maximum removal of

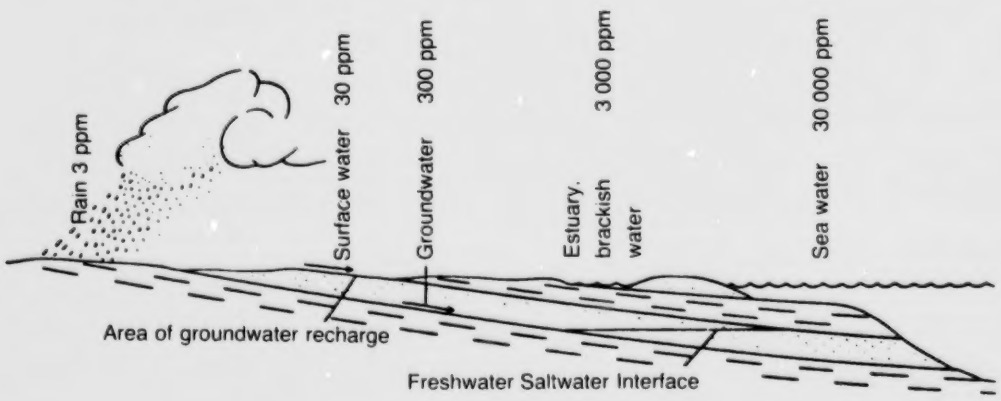

Rain 3 ppm
Surface water 30 ppm
Groundwater 300 ppm
Estuary. brackish water 3 000 ppm
Sea water 30 000 ppm
Area of groundwater recharge
Freshwater Saltwater Interface

FIGURE 3 QUALITY OF WATER IN RELATION TO MODE OF OCCURANCE (Hunt, 1974)

contaminants, the increase in major TDS ion concentrations may lead to corrosion and scaling problems.

Because the chemical composition and concentration of TDS in the effluent from reduced water use processes may be quite different from the intake water it may be necessary to treat the industrial wastewater in order to remove major TDS species prior to discharge into receiving water. These existing problems and the anticipated new problems associated with the discharge of dissolved solids have not been thoroughly investigated and, therefore, are not well understood.

2 SIGNIFICANCE OF TOTAL DISSOLVED SOLIDS IN THE AQUATIC ENVIRONMENT

2.1 Introduction

Natural ground and surface waters are invariably impure and always contain inorganic and organic substances in solution. The types and concentrations of the various impurities are important considerations in the maintenance of water quality for organisms in the aquatic environment. The type of dissolved solids found is important for organisms dependent on natural waters as a principal or sole source for essential nutrients. A significant deficiency of an essential element in a natural water may limit the usefulness of the water for a variety of plants and animals. Excesses of an essential or non-essential element may also limit life due to toxicity. In addition, the overall TDS composition may be significant because it may affect the concentration at which an element becomes toxic. Copper, for example, is an essential trace element which may be limiting if deficient or toxic if in excess. The concentration at which copper becomes toxic to certain species, however, is dependent on the amounts of calcium and magnesium present. To complicate matters further, different species may vary considerably in their tolerance to elemental deficiencies and excesses and, local populations of a particular species may sometimes adapt gradually to levels of a particular substance which may be toxic to populations of the same species elsewhere.

The chemical form of an element or substance in solution may also be important. Aluminum, for example, is least soluble in the neutral pH range and becomes increasingly soluble in an acid or basic medium. The types of dissolved aluminum present in acidic or basic conditions also differs. These different types exhibit varying toxicities.

Even if all of the components of the dissolved solids fraction of a water are present in safe forms, amounts, and ratios, it appears that the overall TDS concentration can be either low or high enough to produce physical stress on some organisms. All dissolved salts alter the physical and the chemical properties of the water solution. Some investigators suggest that the physical changes in the solution which result from different TDS levels and influence osmotic pressure, may be more harmful in many natural situations than toxicity due to the individual elements. Again, tolerance to such physical stresses appears to vary among organisms. While a number of sea dwelling organisms cannot survive in freshwater and some freshwater organisms cannot tolerate TDS levels approaching those of seawater, other aquatic organisms such as salmon and eel, are able to move safely between both.

2.2 Plankton and Aquatic Plants

Allen and Arnon (1955) suggested that optimal growth of the freshwater blue-green algae, *Anabaena cylindrica* occurred at a sodium (an essential nutrient) concentration of 5.0 mg/L. In contrast, Batterton and van Baalen (1971) reported that 1 mg/L sodium chloride (NaCl) met the growth requirements of blue-green algae while higher salt concentrations inhibited growth. They further stated that inhibition was caused more by ionic stress than by osmotic stress even though the latter has been more frequently identified as the cause of inhibition in other studies. Most of the literature also supports the conclusion that the osmotic pressure of the solution is responsible for observed changes in productivity following an increase in salt concentration (Schmidtbauer and Ried, 1967).

Blinks (1951) suggested that most of the osmotic pressure of algae cell sap was due to the common inorganic salts such as sodium and calcium but that little injury resulted from balanced TDS changes because the internal salt concentration of the algae changed passively with the salinity changes of the environment.

In another group of studies using the same species depressed nitrogen fixation in *Anabaena cylindrica* resulted from sodium deficiency (Brownell and Nicholas, 1967). Other species of algae *Anabaena variabilis* and *Synechocystis aquatilis*, were reported to tolerate NaCl concentrations of up to 23.5 percent (235 000 mg/L) while *Microcystis firma* tolerated levels up to 60 percent (600 000 mg/L) (Schiewer, 1974).

Algae which were tolerant to high salt concentrations exhibited greater internal salt and nitrogen concentrations, decreasing carbohydrate content and lower carbohydrate to nitrogen ratios. Pigment content and the production of extracellular carbohydrates were not influenced by the NaCl concentration. Algae which were tolerant to lower levels of salt showed the opposite characteristics (Schiewer, 1974).

Provasoli (1969) proposed that monovalent ions may favour the growth of blue-green algae since this group has a need for sodium and potassium which is not shared by other freshwater algal groups.

In comparison to these freshwater algae studies, a number of studies of marine algae suggest that most unicellular marine algae are tolerant of a wide range of balanced ion salinities, although generally their preference is for lower salinities (Braarud, 1951; Droop, 1958; Gibor, 1956; Provasoli et al., 1954; Ryther, 1954). Blinks (1951) observed the growth of marine algae on the hulls of ships which move regularly from freshwater to saltwater and back. He concluded that most of the larger marine algae species cannot

tolerate dilutions below 0.5 times or concentrations of more that 1.5 times that of seawater. Since the main difference between seawater and freshwater TDS is the sodium chloride concentration, this also suggests a significant tolerance to pronounced sodium chloride changes.

In other marine algae studies, McLachlan (1961) reported a direct relationship between salinity and the growth and relative chlorophyll concentration per cell of *Platymonas sp.*, *Syracosphaera carterae*, *Monochrysis lutheri*, *Olisthodiscus sp.*, *Thalassiosira decipiens*, *Cyclotella sp.*, *Cryptomonas sp.*, *Amphidinium carteri*, and *Porphyridium sp.* at various salinities from 2.5 to 35 parts per thousand in an enriched seawater medium. All of these organisms grew well in a wide range of salinities. Growth was completely suppressed only at the lower salinities. *Thalassiosira*, *Cyclotella*, *Syracosphaera*, *Cryptomonas*, and *Monochrysis* did not show a definite salinity optimum for growth, and the chlorophyll content per cell was approximately the same at all salinities. *Olisthodiscus* and *Amphidinium* demonstrated a salinity optimum for growth. The chlorophyll content per cell was also higher at the same optimum salinity that was observed for growth. Growth of *Platymonas* and *Porphyridium* was not significantly influenced by changes in salinity, but the chlorophyll content per cell was affected by salinity changes.

Algae photosynthesis and respiration, which are related to chlorophyll content, were also shown to be influenced by salinity changes (Blinks, 1951; Ryther, 1954; McLachlan, 1961; Levring, 1957). These studies suggested that an increase in respiration or a decrease in photosynthesis resulted in decreased cell salt concentrations for unicellular algae and decreased size of multicellular algae. Provasoli et al., (1954) indicated that at unfavourable salinity levels, some algae will remain viable but cannot undergo cell division.

In summary, studies of freshwater algae indicate that in some situations the same species of algae are able to tolerate different levels of sodium chloride and TDS and that their tolerances may vary from situation to situation. There is no simple general explanation for this. There is also disagreement about whether specific ionic constituents or overall TDS levels which change osmotic pressures are more significant. In contrast, marine algae are much more tolerant of high NaCl levels and appear to be able to survive in the short-term, through a range of TDS levels. However, they also tend to have preferred long-term ranges of salt concentration.

An increase in TDS could result in more nutrients becoming available, increasing the biological productivity of the water to a certain point. This requires

organisms to adapt osmotically to the new external environment. Most of the osmotic pressure of the algal sap is due to inorganic salts, so if the internal concentration can change without organism stress, little or no population injury may occur (Blinks, 1951). For some groups of algae, however, respiration rates may be affected by changes in salinity to the point where stress occurs, at levels which do not appear to stress other species. Further increases in salt concentrations may eventually inhibit all production resulting in decreased water productivity. This may be first manifested in changes in cellular respiration rate or in decreased cell size or cell division frequency.

The addition of any dissolved substance can also cause shifts in population composition of the primary producers (such as the blue-green algae) which could adversely affect aquatic organisms higher up the food chain. There is close association, therefore, between salt concentrations, primary productivity and the stability of the food chain.

The more complex aquatic plants are very susceptible to changes in the nutrient level of a water body because they depend entirely on dissolved solids for their nutrients (Wetzel, 1974). Kim (1958) reported an inverse relationship between chlorophyll content and salt concentration in higher aquatic plants. *Selanastrum* was inhibited at salinities above 9000 mg/L (Cleave et al., 1976). In another study, inhibition of *Selanastrum* occurred at salinity levels between only 250 and 500 mg/L (Cleave et al., 1976). Investigations of seasonal biomass and nutrient level changes indicated that any overall change in dissolved solids levels will eventually be reflected in the biota (Specht, 1975).

2.3 Macroinvertebrates

The osmotic and ionic regulation in aquatic insects have been studied by a number of authors (Shaw and Stobbart, 1963; Sutcliffe, 1962; Wyatt, 1961). Shirgur and Kewalramani (1973) compared the survival periods of five species of Odonatan nymphs, four species of Heteroptera, and three species of Coleoptera in dilutions of seawater with freshwater (90% to 10% seawater) and in 3.5 percent (35 000 mg/L) solutions of the major TDS constituents of seawater (KCl, KBr, NaBr, $CaCl_2$, $MgCl_2$, Na_2SO_4, $MgSO_4$, $NaHCO_3$ and H_3BO_3). The Odonatan nymphs were the least tolerant while the Coleopterans were the most tolerant of the different seawater dilutions. Of the major ion constituents, potassium chloride (KCl) was found to be the most toxic constituent of seawater and magnesium sulphate ($MgSO_4$) the least toxic for all of the insect studies. In other studies potassium chloride penetrated most readily through the cuticle of *Caliphora erythrocephala*, *Sarcophaga sequirifera*, and *Phoromia regina* compared with other salts.

Richards (1953) reported that, in general, potassium chloride penetrated through cuticle most quickly. Clemens and Jones (1954) determined that crayfish and dragonfly nymphs were the most tolerant of the five invertebrates they tested using sodium chloride (NaCl). In their studies, crayfish would tolerate 17 400 mg/L of NaCl in solution and the nymphs 15 900 mg/L. Lower tolerances were reported for the common ponch snail, *Physia*, (5400 mg/L) the copepod, *Draptomus clavipes* (4300 mg/L), and the water flea, *Daphnia pulex* (2900 mg/L). In comparison, the International Joint Commission (1979) reported that 50 percent of a *Daphnia* sp. population would be killed with 96 hours by an overall TDS level of 4500 mg/L.

Dills and Rogers (1974) observed that increases in dissolved solids in streams adversely affected the invertebrate community. However, the source of the solids was acid mine drainage, which has been shown to contain a number of complex dissolved metal and nonmetal species. Only the hydrogen ion concentration (pH) which could affect the trace constituents could be highly correlated with species diversity.

2.4 Shellfish

Optimum salinity levels have been reported for several species of shellfish; however, the relationship between oysters and TDS levels has been more extensively studied than for any other aquatic species. Although oysters have been found in natural waters with salinity levels from 2700 to 39 000 mg/L, the larger oysters of genus *Crassostrea* appear to prefer much lower salinity levels than the flay oysters *Ostreu*. For example, for the eastern oyster *Crussostrea virginica* and the pacific oyster *Crussostrea gigas*, salinity levels of 18 000 to 20 000 mg/L appear to be satisfactory while the olympia oyster, *Ostrea lurida*, and the american oyster, *Ostrea virginica* prefer higher saline levels. Since oysters usually inhabit an environment which is subject to large daily and seasonal changes, they appear to have developed a remarkable tolerance for salinity variation (Hopkins, 1936). However, freshwater discharges which change the composition of the TDS and reduce overall TDS levels rapidly have been reported to disrupt the feeding, growth and reproduction habits and have also led to mortality. Nelson (1921, 1923) reported that the lowest level of salinity at which *Ostrea virginica* will continue feeding is 10 400 mg/L. Medcof and Needles (1941) reported that oysters stop fattening below 7500 mg/L. In other studies, oysters have reportedly tolerated levels as low as 5000 mg/L for 20 days although shell movement and water pumping were abnormal and growth was inhibited. Massive oyster population mortalities have been attributed to exposure to salinities of less than 10 000 mg/L for more than a few days. Galtsoff (1964)

claimed that the optimum salinity for actively reproducing east coast oyster populations in subtidal areas is 20 000 to 25 000 mg/L, whereas Hopkins (1936) found that the oyster populations he studied preferred salinities in the 26 000 to 35 000 mg/L range.

2.5 Fish

Like the plankton, aquatic insects, and shellfish, fish also appear to differ considerably in their tolerance of TDS levels and TDS constituents. It appears that the osmotic pressure of natural water solutions may be more significant for fish than the toxicity of individual salts observed in high TDS waters. Fish are able to control their internal salinity through osmoregulation and therefore become acclimatized to changes in salt concentrations. A number of studies have been undertaken to determine the response of fish at different life cycle stages to exposure to different salinities.

Zeitoun et al. (1973) reported an increase in the minimum protein requirement of rainbow trout *Salmo gairdneri* fingerlings as the osmotic pressure of the water was increased by increased salinity (20 000 mg/L). The increase in the minimum protein requirements of rainbow trout fingerlings with increased osmotic pressure of the water in which they were reared affirms the importance of dietary protein in protecting the internal environment of the fish against a hypertonic external environment. On the other hand, Zeitoun et al. (1974) claimed that coho salmon *Oncorhynchus kisutch* did not require more protein at 20 000 mg/L salinity. The highly saline environment did not appear to stress the coho smolts possibly due to the development of osmoregulating mechanisms. The total serum protein (protein in liquid residue of blood) of rainbow trout fingerlings was not significantly affected by water salinity and dietary protein concentration. Leduc (1972) found similar osmoregulatory effects following short-term exposure to seawater of salmon (*Salmo salar*) collected from the Atlantic ocean and freshwater. Following short-term exposure to seawater, Rao (1971) found maximum rates of oxygen consumption in rainbow trout (*Salmo gairdneri*) at 30 000 mg/L and the lowest rates at 7500 mg/L, at temperatures of 5°C and 15°C. There was no difference in fish activity in freshwater and in water with 15 000 mg/L salinity. Landless (1976) found that rainbow trout could be put directly into seawater if the salinity was reduced to 22 000 mg/L; however, mortalities of one to eight percent resulted.

In other studies on coho salmon (*Oncorhynchus kisutch*) Otto (1971) discovered distinct seasonal changes in the ability of the fish to adapt to salinity. The time required for 50 percent of test fish populations to die when exposed to high salinity increased during the summer, decreased during the fall and rose again through winter and spring as

their seaward migration period approached. Maximum growth rate, food intake, and gross food conversion efficiencies for the young fish occurred at salinities of 5000 to 10 000 mg/L during the pre-smolt period. Conte and Wagner (1965) and Conte et al. (1966) reported that the salinity tolerances of juvenile coho salmon and ocean-going steelhead trout *Salmo gairdneri* were dependent on size.

In contrast to many ocean-going salmon and trout which can adjust to a wide range of TDS levels, most freshwater species are less able to adjust. In water with a conductivity of 1300 µS/cm (~850 mg/L TDS), fathead minnow (*Pimephales promelas*), northern pike (*Esox lucius*) and walleye pickerel (*Stizostedion vitreum*), eggs hatched successfully. In water of 4000 µS/cm (2600 mg/L TDS) the walleye eggs did not hatch; only some of the pike eggs hatched; while the minnow egg hatch did not appear to decrease (Otto, 1971; Peterka, 1972). At 6000 µS/cm (3900 mg/L TDS), no pike survived and at 12 000 µ S/cm (7800 mg/L TDS) minnows did not survive either. In other studies, populations of fathead minnow from North Dakota lakes had TDS concentrations of up to 12 000 mg/L, but died within 40 minutes of immersion in another lake which had 23 500 mg/L TDS (Landless, 1976; Burnham and Peterka, 1975). Growth of fathead minnow populations was observed to be faster in lakes with a mean TDS concentration of 3250 mg/L than in lakes with TDS concentrations of 1060 mg/L.

On the basis of several studies, Peterka (1972) and Burnham and Peterka (1975) concluded that the ionic composition of the TDS of water appeared to be more important to fish survival than TDS concentration. For example, fathead minnows did not survive in Nebraska lakes which contained more than 2000 mg/L TDS in contrast to the North Dakota minnow populations and Saskatchewan minnow populations which survived in 15 000 mg/L TDS lakes. The Nebraska lake waters had high sodium bicarbonate and sodium and potassium carbonate levels, whereas the North Dakota and Saskatchewan Lakes contained high levels of sodium and magnesium sulphate (Held and Peterka, 1974; McCarraher and Thomas, 1968). Lutz (1972), on the other hand, concluded that osmotic rather than ionic stress determines the lethality of the medium because perch (*Perca fluviatilis*) remained osmotically balanced in waters ranging up to one third the TDS level of seawater. In water of approximately one half the TDS content of seawater the fish were no longer able to continue osmoregulation.

Tolerance of catfish to various TDS concentrations was the subject of another group of studies. The channel catfish (*Ictalurus punctatus*) and the blue catfish (*Ictalurus furcatus*) have been found in waters on the Gulf of Mexico with salinity levels up to 11 400 mg/L (Perry, 1967). Stickeny and Simco (1971) found that hybrids of these catfish

could tolerate 96-hour periods in water of 14 000 to 15 000 mg/L salinity. Allen and Avault (1971) reported that blue catfish were more tolerant of 14 000 mg/L salinity than channel catfish. Perry and Avault (1968) demonstrated the survival of channel, blue and white (*Ictalurus catus*) catfish in brackish pond waters of 2000 to 11 000 mg/L salinity. Kendall and Schwartz (1968), however, determined that after 60 hours in 14 000 mg/L salinity water, 50 percent mortality in a population of white catfish occurred. Similar results were reported in another study with some observations of individual ion effects (Goudie and Davis, 1978). It was suggested that calcium reduced the adverse effects of high salinity on channel catfish and that the cardiac and opercular opening rates of channel catfish increased with increasing phosphate concentrations up to approximately 12 mg/L phosphate (Strange et al., 1978).

In studies of buffalo fish (*Ictiobus* sp.), preferences for different salinity levels by closely related species were also demonstrated. Hollander and Avault (1975) reported that hybrids of the bigmouth buffalo fish (*Ictiobus cyprinellus*) and black buffalo fish (*Ictiobus niger*) could tolerate salinities up to 9000 mg/L while Perry (1976) found that salinities of 1600 to 1800 mg/L were most suitable for the black buffalo fish and salinities of 1400 to 2000 mg/L were optimal for the bigmouth buffalo fish.

In other studies, Rao (1974) suggested that a salinity range of 5000 to 14 000 mg/L is the physiological optimum for the California killifish (*Fundus parvipinnis*) while Clemens and Jones (1954) reported that Plains killifish (*Fundus kansae*) could tolerate much larger increases in sodium content if they were living in waters of relatively high chloride content than if they were living in waters of low chloride content. Chittenden (1973) demonstrated that young American shad (*Alosa sapidissima*) could tolerate very large salinity increases when going from freshwater to saltwater but suffered severe mortality when exposed to abrupt decreases. Finally, Heeg (1975) reported that aquatic snails, which would die if exposed rapidly to significantly higher TDS levels in freshwater than they were used to, could be successfully acclimated to the same levels without mortality if the TDS levels were gradually adjusted upwards.

2.6 Biological Communities

It appears from the literature that in general, the regular, cyclic, naturally occurring changes in levels of dissolved solids seldom result in drastic, acute, or immediate effects on the biological communities. Drastic, permanent changes in dissolved solids are rare in naturally occurring freshwater because the concentrating and diluting effects of evaporation and inundation will, under normal circumstances, be

gradual. The effects are usually subtle and seldom completely eliminate or significantly stimulate biological systems. On the other hand, all changes in dissolved salts do alter the physical and chemical nature of the water, and exert osmotic pressure. The harmful environmental effects observed from high TDS levels are generally attributed to high osmotic pressure and not the toxicity of the individual salts. This assumes that the dissolved solids solutions are composed primarily of the commonly occurring constituents of natural waters and that they are present in suitable proportions with the different ions counteracting each other. A deficiency or excess of certain ions or both may be biologically limiting. Active transport of dissolved solids through the cell wall and into the surrounding medium is required for the maintenance of an acceptable intracellular environment. The relationship between osmotic stress and increases in ionic concentrations, therefore, should be considered when determining safe TDS levels for communities of organisms.

The addition of any amount of dissolved solids which causes shifts in population composition of the primary producers could adversely affect aquatic organisms further up the food chain. Because of the close association between dissolved solids, nutrient availability and the growth of aquatic organisms, future water quality considerations for TDS should take into account biological effects on the food chain and community in the water body as well as on individual populations.

Often, it is not feasible to use the presence or absence of organisms or number and diversity of species as an indicator of the effects of dissolved solids since some resistant form of life will likely be present (Tillman, 1981).

Although some research efforts have been directed at determining the effects of dissolved solids on freshwater ecosystems, there are still significant gaps in the data about the effects on lower organisms and also at the community level and community responses.

Acute effects of TDS changes on specific organisms which result in subsequent community changes have been difficult to demonstrate. Succession and adaptation can allow communities to be maintained even though specific organisms may differ. Consequently, Sorensen et al. (1977) concluded that the total quantity of dissolved salts and the composition of the common ions are both important in terms of organism type, selection and productivity in the aquatic environment. The mode of action of dissolved salts is primarily due to to osmotic interactions if TDS composition is relatively balanced. Cation and anion ratios seem to have important roles in succession of certain organisms. A major assumption concerning the osmotic effects on the aquatic environment is that the major

constituents will remain in balance with certain limits. Only at this point do osmotic effects warrant consideration. Further evidence suggests that when this balance no longer holds, deleterious physiological effects may be observed.

Although fish adapt somewhat to gross changes in salinity, life cycle effects may prevent certain fish from surviving in specific aquatic habitats. Osmoregulation is an important aspect of adaptation. Biochemical changes such as protein and glucose levels in the blood are indicators of salinity changes.

Impacts of changes in common dissolved solids or TDS levels and the concentrations of individual salts on the physical and chemical characteristics of water are well understood. However, biological responses appear to vary from organism to organism and are less understood. Biological responses at the community level appear to be the least understood and, unfortunately, these responses which affect diversity, successional processes, energy transfer and food chains in the ecosystem are most relevant for the determination of safe water quality levels.

In the literature, there are many contradictory observations on the effects of TDS changes on aquatic species. Some of these have been mentioned as examples. Reviews of this type often lead to the conclusion that the organism and community response to changes in TDS concentrations are complex and are site and organism specific. It must also be noted, however, that it is frequently difficult to compare the specific chemical changes which have been reported in the literature to cause adverse or stimulative effects since researchers have often not cited the method used for their TDS determinations or the complete chemical constituents of the TDS. A significant reason why more general statements about TDS and organism responses cannot be made may be due in part to shortcomings in the chemical characterizations or assumptions about TDS constituents in many of these investigations.

Since assumptions of major ion composition are often not clearly stated or the methods used to measure individual chemical species are not provided, a number of the studies reported in the literature tend to be of limited usefulness other than as site and/or species specific references. Similarly, studies of this nature are of very limited value if extrapolation to the evaluation of industrial effluents of difference dissolved solids concentrations is desired.

3 TOTAL DISSOLVED SOLIDS: CHARACTERIZATION AND DETERMINATION

3.1 Introduction

In this section common definitions of total dissolved solids and several of the methods used to quantify TDS concentrations are presented. Several examples which illustrate the differences between analytical methods and the problems which can arise from these differences are described.

3.1.1 Definition of Total Dissolved Solids. Solids which occur in water are classified depending on the nature of the water and solids of interest. Most commonly they are classified as either dissolved or particulate (suspended) substances. This classification may be subject to misinterpretation since it is based on working procedures or analytical methodologies which may not entirely correspond to theoretical or colloquial definitions. For example, dissolved solids are often considered to be comprised of only ionic salt species such as carbonate, chloride or sodium. Depending on the analytical procedure used, however, dissolved solids may be comprised of much more than simple electrolytes of this type. Dissolved solids, as measured by the evaporative or gravimetric procedure consists of all material which passes through a standard glass fibre filter paper with a pore size of 1 µm and remains after evaporation and drying to a constant weight. Materials which are measured include all ions, organic molecules and some colloids. The total dissolved solids measured by Standard Methods using the evaporative procedure may be quite different from those measured by other means or from the meanings intended in colloquial definitions.

3.1.2 TDS Composition. The composition of dissolved solids in natural water has been the subject of much study. Several researchers have indicated that the major constituents of most natural waters contain the same few inorganic anions and cations (Livingston, 1963; Meybec, 1976; David and Dewiest, 1966; Kobayashi, 1960). Livingston (1963), for example, calculated the weighted mean concentrations of various constituents of rivers and lakes in several continents (Table 1). David and Dewiest (1966) and Hanya (1953) presented cumulative frequency curves showing the distribution of various constituents in potable waters from the United States and from river and near surface groundwaters in Japan. The ranges of concentrations of major ions determined in these studies are shown in Figure 4.

Based on several such studies, the major dissolved solids of natural waters are generally considered to be the cations Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+} and the anions HCO_3^{-},

TABLE 1 MAIN DISSOLVED SOLIDS OF RIVER WATERS FOR THE WORLD (Livingston, 1963)

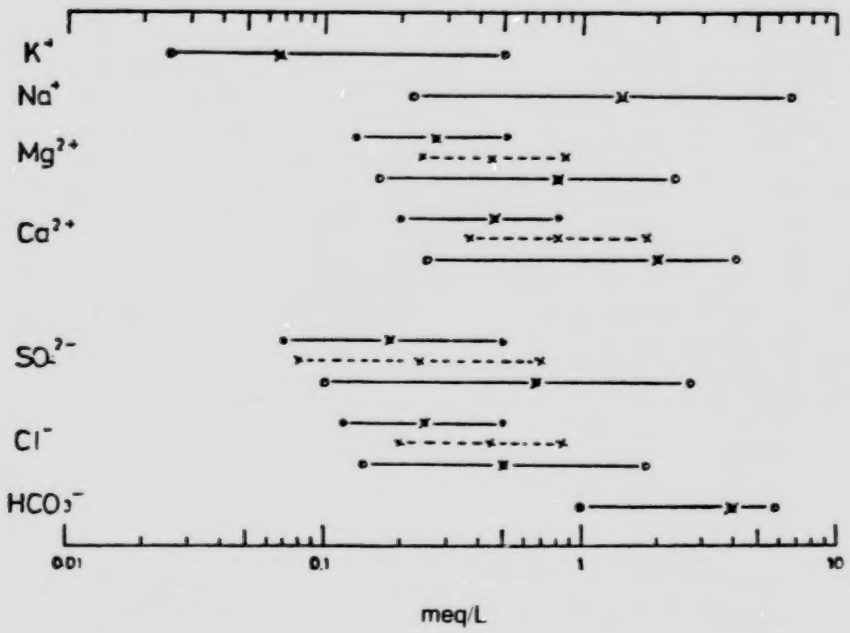
Parameters	Concentration (mg/L)
HCO_3	58.4
SO_4	11.2
Cl	7.6
NO_3	1
Ca	15
Mg	4.1
Na	6.3
K	2.3
Fe	0.7
SiO_2	12
TOTAL	118.6

Cl^- and SO_4^{-2}, as well as silica which is usually in the non-ionic form. The concentration of K^+ is often very low compared with the others.

Most natural waters contain a much broader range of dissolved solids species than those previously listed. These additional species, however, tend to be present only in trace individual amounts which collectively, tend to make up a small portion of the TDS. These additional solids reflect the natural geology and mineral cycle differences in specific regions.

Cottenie and Dhaese (1978) found the occurrence of trace heavy metals in freshwater was strongly related to the presence of the metals in soils and sediments. These metals are often present as organo-mineral complexes. They are formed by reaction of metals with fulvic and humic acids and other organic matter resulting in complexes of varying stability and solubility. These species concentrate as a function of the local chemical conditions since the transfer from the solid to liquid phase is largely dependent on factors such as pH, reduction-oxidation potential and organic matter.

Other waters which have been influenced by various forms of industrial wastes sewage or agricultural by-products can contain a great variety of dissolved solids species



- o river water of Japan
- x near surface water of Japan
- ● potable water of the United States

FIGURE 4 RANGES OF THE CONCENTRATION OF MAJOR DISSOLVED SOLIDS CONSTITUENTS IN NATURAL WATERS (David and Dewiest, 1966; Hanya, 1953)

which are not related to natural local conditions but to the specific processes, materials and wastes.

3.2 Analytical Methods

In practice, the definition of TDS is either arbitrarily assigned or defined by the analytical procedure. Several procedures are described in this section including descriptions of the species measured and the relative limitations of the analytical methods.

3.2.1 TDS by Evaporation. The evaporative method for determination of TDS is one of the most widely used procedures. In the development of other procedures for measurement of total dissolved solids, the assumption is generally made that the new procedure will be used as a simpler substitute for the evaporative method or that it will be used as a means of checking the results of analyses by the evaporative method.

The evaporative procedure described in Standard Methods (1980) has been widely adopted as the standard evaporative method. Often, researchers do not specify the method of TDS analysis when reporting results. In this report, it is assumed that all TDS analyses are completed using this procedure, unless stated otherwise. According to this method total dissolved solids is the material from a well mixed sample that passes through a standard glass fibre filter disk and remains after evaporation and drying under specified conditions to constant weight.

Material which has a significant vapour pressure and may be lost during evaporation will not be defined as a solid. To more accurately reflect this possible loss, the term "filterable residue" is used to describe the dissolved solids measured by this method. The dissolved solid species which will be measured include any particles which will pass through the filter and remain after the evaporation. Factors affecting the filtration and evaporation steps are most notably the filter pore size and the temperature and duration of heating respectively.

The pore size of the filter affects the dissolved solids measured since it ultimately defines the upper limit of particle size which will be included in the filtrate. Generally, a 1 μm pore size filter is used, however, occasionally a 1.2 μm or 0.45 μm pore size filter may be used depending on the circumstances.

The classification and size range of particles relative to the pore sizes are shown in Figure 5. Particles between 10^{-3} and 10^{-5} μm in size including small organic and inorganic molecules and ions would easily pass through the pores. The calcium ion

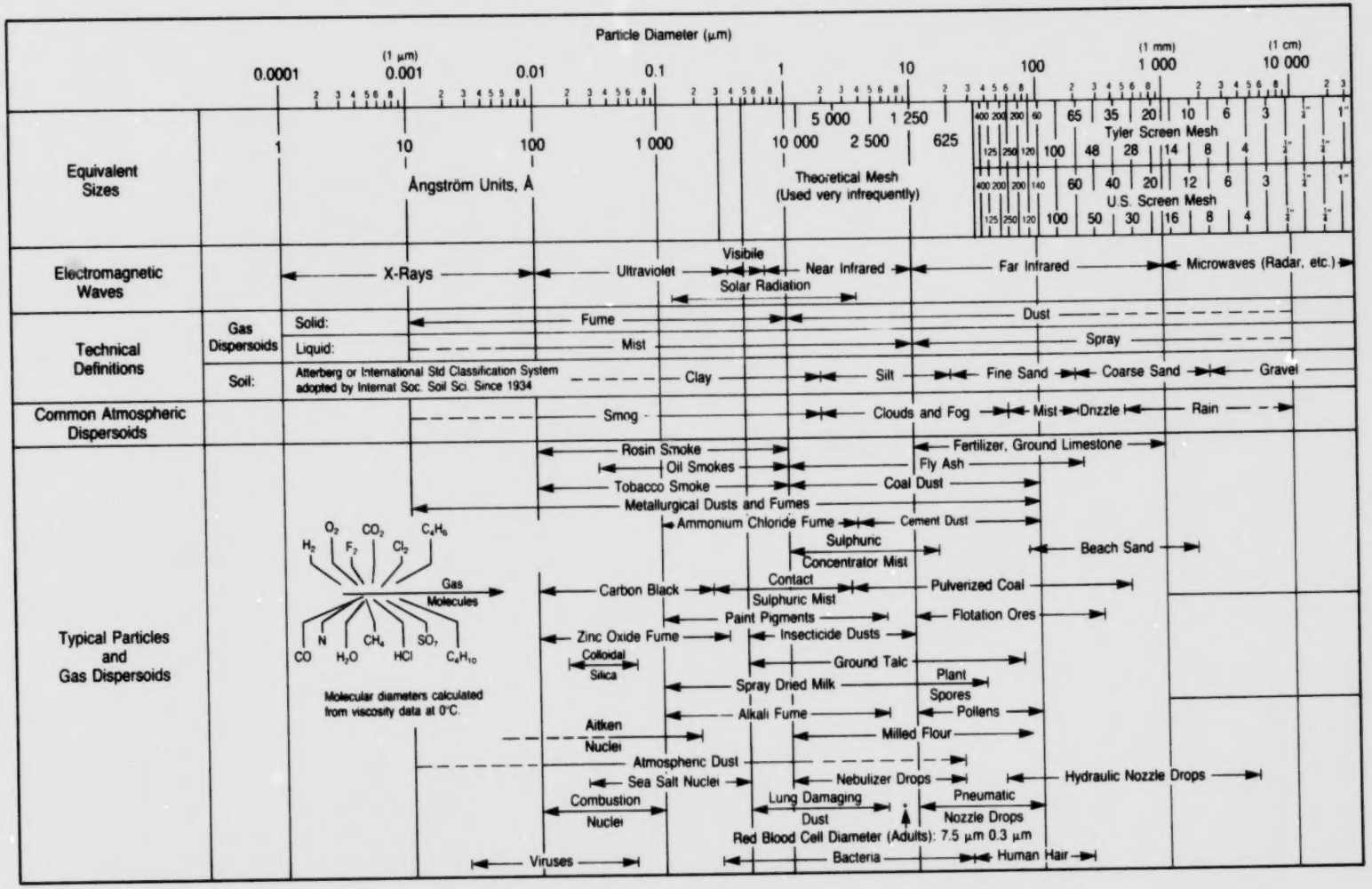


FIGURE 5 CLASSIFICATION AND SIZE RANGE OF PARTICLES (Anon., 1959)

(Ca^{+2}), an inorganic metal ion, has an ionic radius of 0.099×10^{-3} µm and therefore easily passes through the filter disk.

Other particles which can pass through a 1 µm pore size filter are colloids. Colloids are particles or aggregates with diameters ranging from 10^{-3} to 1 µm which remain suspended in the water. Their stability or non-settling character is partly due to their positive or negative electrical charge (McGirr, 1974).

3.2.2 Commercial Filter Media. Filters remove particles by a number of mechanisms, including: direct interception, inertial deposition, diffusional deposition, electrical attraction and gravitational attraction (Stenhouse et al., 1970; Benarie, 1969; Kirsch and Fuchs, 1968; Stechkina et al., 1969; Lundgren and Whitby, 1965; Zebel, 1965; Rimberg, 1969; Lockhart et al., 1964; Spruny et al., 1969; Liu and Lee, 1976). One or more of these mechanisms may predominate in a given situation depending on the flowrate, the nature of the filter, and the nature of the liquid.

Filter media which are commercially available can be divided into four groups by their composition (Cellulose, glass fibre, membrane and nucleopore).

Cellulose filter papers are primarily used for liquid solid separation and are made from purified cellulose pulp. Although they are relatively inexpensive and exhibit high tensile strength they are non-uniform and as a result have variable flow resistance, collection efficiency and hydroscopicity. This makes accurate gravimetric determination very difficult.

Glass fibre filters are usually more expensive and have poorer mechanical properties than cellulose papers. They also have reduced hydroscopicity and have the ability to withstand high temperatures and higher collection efficiencies at a comparable pressure drop. A serious source of error is the loss of filter fibres drawn through the support screen during filtration.

Membrane filters consist of porous membranes which are used where fibrous filters cannot be used. Membranes may be composed of cellulose triacetate, regenerated cellulose, polyvinyl chloride, nylon, polypropylene or teflon. Collection efficiency increases with decreasing pore size, but even larger pore size filters have relatively high collection efficiencies for particles much smaller than their pores. Membrane filters do not behave as sieves. As in fibrous filters, particles are removed primarily by impaction and diffusion.

Nucleopore filters are similar to membrane filters in that they contain both uniform sized pores and a solid matrix. These filters have a smooth filtering surface; the

pores are cylindrical, almost uniform in diameter and perpendicular to the filter surface. The structure is sufficiently simple that it is possible to predict the particle collection efficiency based on particle collection theory (Spruny et al., 1969). This type of filter paper most closely approximates sieve type separation of solids and gives the most uniform particle size cut off.

Regardless of the type of filter paper used, it cannot be assumed that there is a minimum uniform particle size which is trapped by the fitler. For example, a 0.8 µm nominal pore size filter paper will capture all particle sizes greater than 0.8 µm. However, it cannot be assumed that particles less than 0.8 µm will not also be captured. For this reason, filtration cannot be used as a means to differentiate particle sizes.

Other major factors affecting TDS measurement involving filters are the temperature at which the filtrate is dried and the period of heating. The drying temperature and duration will determine the weight losses which may occur due to volatilization of organic matter and loss of occluded water as well as losses of water of crystallization and gases from chemical decomposition. Because of the variation of TDS measurements with temperature, a judicious choice of temperature and drying conditions is necessary depending on the nature of the sample. Temperatures chosen for TDS measurements are 103°C to 105°C, 180°C, and 550°C. Samples are normally dried for a period of one hour or until constant weight is obtained.

Generally, samples which are dried in an oven for one hour at 103°C to 105°C retain most of their organics and water of crystallization. Bicarbonate which converts to carbonate at higher temperatures will not have undergone a complete conversion at this temperature.

Samples which are evaporated at 180°C will lose most volatile organics and water of crystallization and bicarbonate conversion to carbonate will be almost complete.

Occasionally, samples are evaporated at 550°C $\pm$ 50°C in order to drive off the water of crystallization and organics with the intention that only the inorganic residue will remain. This is only an approximation, however, as losses due to volatilization of certain inorganic salts in addition to organics will occur at this temperature.

The main problem with the evaporative method of TDS determinations is that the solid material deposited when a water sample is evaporated to dryness does not completely represent the material that was originally in solution and therefore the dry weight of material expressed in mg/L will not coincide with the amount of material originally present.

Some of these changes which result because of the analytical procedure used have already been mentioned. Dissolved gases which are important in characterizing a water will be driven off. Bicarbonate which converts to carbonate results in the loss of H_2O and CO_2 as shown:

$$2HCO_3^- \rightarrow CO_3^{-2} + CO_2 + H_2O$$

Some solid salts may be volatile at the temperature chosen. This effect is most noticeable in waters of high magnesium, chloride and nitrate content owing to the decomposition of magnesium salts. Water of crystallization may also be lost or gained during evaporation resulting in a lower or higher measurement of water of crystallation than was chemically active in solution. These factors are possible sources of error and as a result the accuracy of the method is difficult to assess.

A study conducted by the Inland Waters Directorate of the Environmental Conservation Service, Environment Canada, involving 18 laboratories, indicated that the relative standard deviation of the total dissolved solids determined as residue in mg/L ranged between 7.0 and 15.0 percent. A relative error of 13 percent was obtained (McGirr, 1974).

3.2.3 TDS by Conductivity. Electrical conductivity also known as specific conductance has been widely used as a measure of water and wastewater quality. This method is an immediate and convenient instrumental means of determination and has been widely used to indirectly measure the TDS of water.

Water contains dissolved solids which are in the form of ions, colloids and organics. Ions such as Cl^-, SO_4^{-2} and NO_3^{-2} act as electrolytes in water and are able to conduct electricity. Conductivity is a function of the specific conductance of each individual ion, the concentration of each ion and the temperature. Because these electrolytes in solution can be measured by their conductance, the values obtained can be related to the dissolved solids of a water.

Specific conductance is a measure of how well ions transmit current and is dependent on their mobility and valence. Table of specific conductance values are available for different ions. Dissolved solids can be calculated from conductivity measurements when only one species of ion is present in solution.

The electrical conductivity also depends on the number of ions present in the solution. The more electrolyte present, the greater the conductivity of the solution. This can be misleading, however, when electrolytes composed of a number of chemical constituents are considered. For example, when a given electrolyte with a high specific

conductivity predominates, the conductivity of that wastewater will be high. If in another wastewater a different electrolyte predominates which has a low specific conductance but the concentration of total electrolytes is the same, then the conductivity of the solution will be less.

An alternating current Wheatstone bridge attached to two electrodes in the conductivity cell is used to measure conductivity. Alternating current is used in order to eliminate polarization effects which occur because ions in solution would be attracted to the electrode of opposite charge causing a high resistance at the electrode surface which would mask the conductivity measurement. When the electrodes are immersed in solution and a voltage applied, a current flows between the electrodes. The resistance created by the ionized solution is measured by the Wheatstone bridge circuit, amplified and converted to units of conductivity.

The ability of a solution to transmit a current depends primarily upon the concentration of ions, expressed as ions/cm^3. Electrolytic conductivity or specific conductance is defined as the reciprocal of the resistivity in ohm - centimetres of a one centimetre cube of solution at a specified temperature. The units of measurement are reciprocal ohm · cm or mho/cm (S/cm). Pure water has a conductivity of 0.055 µS/cm and a good quality raw water about 100 to 200 µS/cm. Seawater has a conductivity of about 50 000 µS/cm.

Temperature also affects the electrical conductivity of a solution. The conductivity of a solution almost always increases with increasing temperature. This is shown in Figure 6 for a 0.01 N solution of KCl. As a solution is heated the conducting ions become more mobile and "carry" a charge more easily. In practice temperature must be compensated for and most conductivity instruments are equipped to do so automatically.

Several researchers have attempted to relate the conductivity produced by ions in solution to dissolved solids concentrations. Generally, conductivity measurements related to dissolved solids via a factor (f) (see Table 2):

$$\text{Dissolved solids} = f \times \text{electrical conductivity}$$

The factor is often obtained by a linear regression analysis of plots of dissolved solids as measured by evaporation versus specific conductance. Once the factor is known, it may be used directly to relate further conductivity measurements to total dissolved solids of similar types of water. The factor obtained is specific for water of a particular region and composition.

TABLE 2 VALUES RELATING TOTAL DISSOLVED SOLIDS OR EVAPORATED RESIDUES (mg/L) TO ELECTRICAL CONDUCTIVITY

Factor	Reference
0.6	(Hanya, 1960)
0.55 to 0.7	(APHA, 1965)
0.64	(Todd, 1959)
0.7	(David and Dewiest, 1966)
0.69	(Taylor, 1958)
0.72 to 0.73	(Suzuki, 1964)
0.63	(Lystrom, Rinella and Knox, 1978)

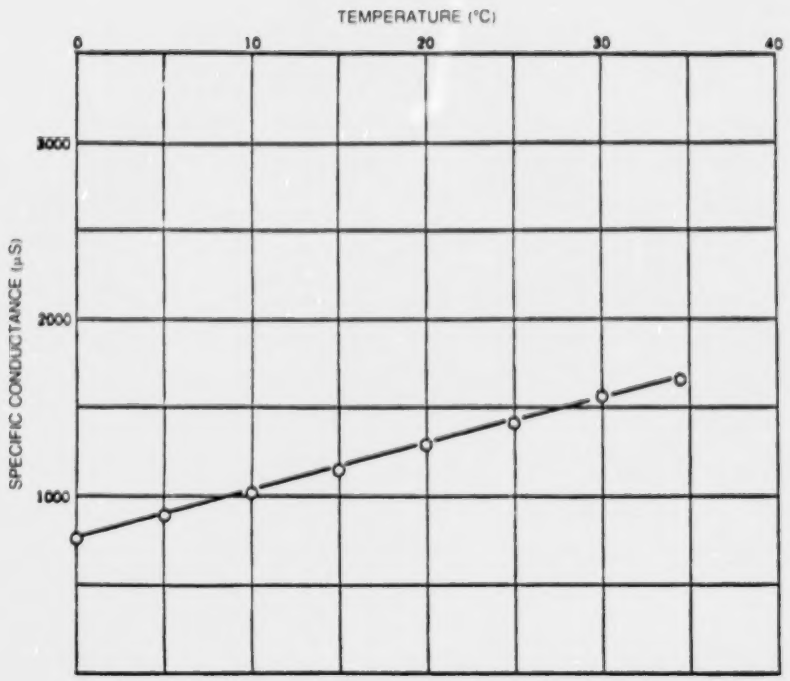


FIGURE 6 SPECIFIC CONDUCTANCE AT VARIOUS TEMPERATURES (0.01 N KCl solution)

Attempts have been made to develop a general equation relating electrical conductivity to dissolved solids. Tsurumaki (1974) related electrical conductivity to dissolved solids expressed as total ionic sums (half the sum of anions and cations) by taking the variations of concentration and composition in water samples into consideration. Calculated values were compared with analytically determined values for a wide variety of natural waters. This relation was not applicable to samples which contained significant amounts of uncommon ions such as borates or a high total concentration of ions.

A regression analysis technique was applied to 1441 paired values of dissolved solids concentrations and specific conductances for the Susquehanna River Basin in Pennsylvania (Lystrom et al., 1978). Using this data, Lystrom et al. (1978) obtained the relation:

$$Y = 0.626\ X$$

where Y = the dissolved solids concentration

X = specific conductance

The standard error of estimate of the calculated equation was $\pm$ 16.6 mg/L or $\pm$ 10.5 percent of the dissolved solids concentration. Errors resulting from use of a regional model at some stations were found to be significantly greater than errors resulting from station models.

Generally, this relationship between electrolyte and conductivity is linear, however, it becomes non-linear at higher concentrations due to a decrease in ionic velocity resulting from inter-ionic forces. Other effects such as electrostatic attraction between ions in solution and variations in dissociations of weak acids and bases, depending on their concentration, may affect the linearity at lower and intermediate concentrations.

Calculation of total dissolved solids by conductivity measurements requires a different regression line for each region when dealing with natural or surface water from different regions or for each different wastewater in industrial plants. For this reason, a universal factor relating conductivity to dissolved solids does not exist. The problem of selecting a factor exists even with general relationships which have been established, particularly when extensive water characterization has not been completed to determine the presence of any uncommon ions.

Also, inherent in the method is the limitation of total dissolved solids estimations to waters which contain only good conductors such as inorganic acids, bases and salts. Waters which contain dissolved solids, comprised of organic compounds which

do not dissociate in water and conduct a current very poorly, do not lend themselves to this method of dissolved solids determination.

3.2.4 Measurement of TDS Using Refractive Index Measurement. Refractive Index measurements have also been used as a means of determining total dissolved solids content. The method is more direct and less time consuming than the evaporative procedure. It has been used in the continuous monitoring of influents and effluents of a number of sewage treatment plants (Liskowitz and Huang, 1974).

Refractive indices of a substance are numbers obtained from the ratio of the speed of light in air to the speed of light in the substance. Using these indices, the extent by which various substances cause a decrease in the speed of light as compared with its speed in air or a vacuum can be expressed. The decrease in speed depends on a number of factors including the wavelength of light, the temperature, and the chemical composition and purity of the substance. The relationship between concentration of solutions and refraction is of particular interest here.

The fundamental basis of refractive index measurement is the phenomenon of refraction. When light of a specific wavelength travelling through medium 'G' is incident at an angle 'i' with the normal or a plane interface between 'G' and a second optically denser medium 'L', then part of the light enters 'L' and proceeds at a corresponding angle 'r' with the normal (Figure 7). The relationship between the velocity in medium G (v) and L (v') is given by:

$$v \sin r = v' \sin i$$

For various values of the angle 'i' the ratio of the sine of the angles of incidence and refraction is a constant:

$$n = (v/v')$$

The value 'n' is the refractive index of medium 'L' with respect to medium 'G' for light of a given wavelength.

Air is customarily used as medium 'G' and is the standard with respect to which of the refractive indices of liquids are expressed.

Conditions such as temperature and pressure must be controlled when primary standards of index are being determined. Tables of reference standards which are used in the calibration of refractometers are available for homogeneous solids and liquids.

With most ordinary refractometers, variations in temperature will cause variations in measured refractive indices. Generally as temperature increases the density

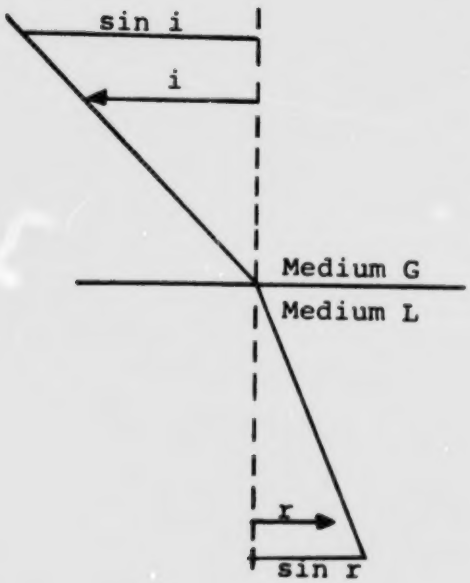


FIGURE 7 REFRACTION OF LIGHT

of a material decreases yielding a lower index of refraction. Other phenomena such as the capacity for adsorption of radiation of longer wavelength causing an adsorption "shift" in the ultraviolet range are temperature dependent and can result in varying indices of refraction (Tilton and Taylor, 1960). Numerous published data are available concerning the refractive index changes with temperature for liquids and show that the effect due to density predominates.

Temperature problems concerning refractive index measurements are overcome with the use of a differential refractometer. With this instrument, known and unknown samples are placed in the instrument together to permit temperature equilibration. The refractive indices are then compared simultaneously. The value obtained using a differential refractometer is called the differential refractive index and is equal to the difference of refractive indices of the sample and reference solution. In dealing with water solutions the reference solution is usually distilled water.

For many aqueous solutions containing a single solute, the index is found to be a linear function of the concentration and is practically independent of temperature when the concentration 'c' is expressed in grams of solute per 100 mL of solution.

In the optical system of the differential refractometer light passes through a series of optics, a spectrometer slit, a differential cell, a lens, and finally a micrometer microscope. All parts are carefully aligned on an optical bench.

The fine beam of light emerging from the slit is refracted through the differential cell and viewed through the microscope. The displacement of the spectrometer slit image is determined by carefully focusing the microscope and centering the cross-hair on the slit image.

The difference in refractive index (n) between solution and solvent is strictly proportional to the total measured displacement (d) of the slit for a given solution as shown in the following equation:

$$n = h \cdot d$$

The constant 'h' can be determined either geometrically or by means of solutions of known refractive index.

Liskowitz and Huang (1974) studied the measurement of TDS by differential refraction on sewage samples from New Jersey treatment plants. They also determined inorganic dissolved solids using conductivity measurements and used the difference in results between these two measurements to determine the concentration of dissolved organic solids.

Gravimetric determination of total organic and inorganic dissolved solids were performed according to standard procedures (APHA, 1980). The relationship between differences in refractive indices of influent and effluent sewage samples and water and the concentration of total dissolved solids as determined using gravimetric procedures, is shown in Figure 8. The linear relationship between differences in refraction indices and distilled water for samples before and after removal of suspended solids and total dissolved solids shows reasonable agreement as indicated by the dotted line.

The researchers concluded that for the sewage samples examined, the differential refractive index measurements could be used to determine the TDS concentration in waste streams. The linear relationship between differences of refractive indices and total dissolved solids appeared to be independent of the suspended solids concentrations, colour and composition of the dissolved solids present in the water.

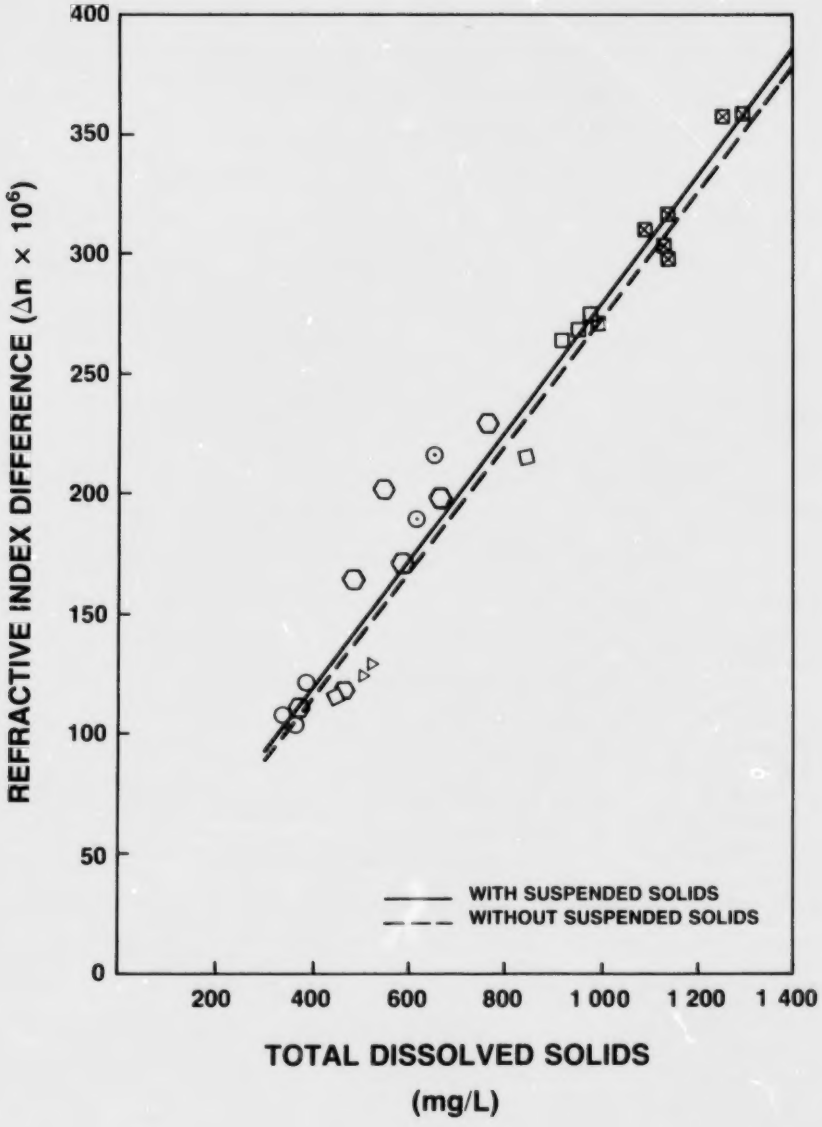


FIGURE 8 RELATIONSHIP BETWEEN REFRACTIVE INDEX DIFFERENCE AND TOTAL DISSOLVED SOLIDS FOR SEVEN DIFFERENT WASTE TREATMENT PLANTS IN NEW JERSEY (Liskowitz and Huang, 1974)

Other applications for refractive index measurements include the determination of concentrations of sugar solution (Brice and Hawler, 1951). Solutions of a number of sugars and related substances have approximately the same refractive index for equal percentage compositions by weight. As a result, this method can be used to determine the amount of soluble carbohydrate in a solution or the amount of a given species if the solution is known to be pure.

The measurement of small differences in the refractive index of liquids has also been used in the determination of colourless solutes in dilute solutions. Clemens (1921) has discussed the use of the emersion refractometer in the determination of solutes from a knowledge of density and refractive index of the aqueous solution.

Refractive index measurements have been shown to offer a simple, quick and reliable means of measuring total dissolved solids. The concentration 'c' of dissolved solids may be obtained from the relation:

$$\frac{Wn}{b} = c$$

when the total dissolved solids concentration is made up one chemical constituent. The constant 'b' is calculated from measurements of the change in refractive index for a known concentration of the solute of interest and tabulated values of indices of refraction.

If the dissolved solids consist of several constituents, a standard curve must be prepared comparing the differences in refractive index (Wn) with the total dissolved solids as determined by standard gravimetric procedures. This must be done in order that the content 'b' may be determined, assuming the relationship between 'n' and 'c' is linear. The first approach requires the composition of the solution to be known. The second approach requires that the dependence of the index of refraction on the concentration be determined analytically. Thus each distinct wastewater type must be studied in order to prepare the curve relating refractive index measurement with the concentration of total dissolved solids.

The method of refraction has not been widely used for the determination of dissolved solids except for determination of sugar concentrations in water, possibly due to the need for stringent characterization of the particular water as noted. The method also requires very precise optical measurements to be made as well as very careful alignment of the instrument which would not lend itself to situations where only coarser analytical techniques are needed.

3.2.5 TDS Specific Gravity. Approximate values of total dissolved solids may be obtained from specific gravity measurements. The relationship between density and concentration of even simple salts in solution is complicated, however, several expressions have been developed to define this relationship.

Dissolved solids generally change the density of specific gravity of a solution in direct proportion to their concentration. The magnitude of the change depends on the nature and amount of dissolved solids present. The density of a fluid is the mass of the fluid per unit volume and is obtained by weighing the mass of a known volume of liquid. Specific gravity is the ratio of the density of a specific volume of solution to the density of an equal volume of water.

Generally, measurements are made by weighing a container or conventional density bottle and then filling the container to a specified volume with the solution and reweighing the container and solution. The container is then weighed when filled with the same volume of water. Specific gravity is then calculated from the formula:

$$\text{specific gravity} = \frac{A_1 - B}{A_2 - B}$$

where A_1 = weight of bottle plus sample
A_2 = weight of bottle plus water
B = weight of the bottle

Alternatively, specific gravity may be determined by using a hydrometer. A hydrometer is a weighted float with a small diameter stem at top. The float sinks in liquid to a depth proportional to the specific gravity and a scale inside the float is read at liquid level. Values of specific gravity obtained are then compared with total dissolved solids determined using standard gravimetric procedures. Methods of making specific gravity measurements have been summarized by Strouts et al. (1955) and Partington (1955).

The relationship between the concentration of dissolved salts and water density has been studied by several researchers. Studying solutions of common table salt (NaCl), Gaehr (1911) derived the equation ($\log d = mc$) to described the relation between density (d) and concentration (c) in percent, where 'm' is a constant. The equation was then applied to a number of other salts and some acids but it could not be universally applied. For plots of density versus concentration, three classes of curves were obtained:

(a) straight lines (this includes those curves which differed by a maximum of 0.6 percent from a straight line);

(b) curves sloping uniformly upward or uniformly downward; and

(c) curves with double curvature.

A single equation relating density to concentration of all species studies was not obtained.

Solutions whose maximum TDS concentrations were less than 15 percent obeyed the equation (log d = mc) very well. A partial explanation of some of the anomalies observed when relating density to concentration is shown by the effect that charged ions in solution have on the volume of solvent. As a consequence of increased ionization when a solution is diluted there is an effective change in volume due to electrostriction. Masson (1929) studied the relation between the volume of a solution and the concentration. He derived an equation to explain the relation but found certain deviations which may be due to the change of coordination of water molecules in the presence of ions. This can occur where the volume of $MgSO_4$ solution is less than the original volume of solvent after the dissolution of the salt.

Dissolved gases have only a slight effect on the specific gravity of water. For example, when CO_2 is dissolved in water the solution expands. The change in specific gravity, however, is negligible at 22°C.

The relationship between density or specific gravity and concentration is complex. Due to the presence of a wide variety of salts at various concentrations, a definitive expression relating the total dissolved solids and the density of surface water is not likely.

Agnihotri and Tewari (1968) obtained a relationship between specific gravity and total dissolved salts in a number of surface and subsurface water samples. They found that the empirical equation TDS = (specific gravity - 1) f where 'f' is a common factor, described this relation. Specific gravity values were obtained using 50 mL capacity density bottles as described earlier. Temperatures were maintained at 20°C to 22°C. The total dissolved solids of each sample was obtained using the usual gravimetric procedure. Samples were dried at 180°C for one hour. There was some doubt expressed as to the accuracy of the gravimetric results because $MgSO_4$, present in some solutions, remained hydrated at 180°C and as a result a constant weight could not be obtained. Also of concern were $Ca(CHCO_3)_2$ and $NaHCO_3$ which partially decomposed at this temperature.

The values of 'f' obtained using the equation varied between 100 and 150 for the 150 groundwater samples studied. About 90 percent of the water samples had values of 'f' between 115 and 135. A closer examination was directed between the 115 and 135 range. The chief cations and anions in the groundwaters studied were Na^{+}, Ca^{+2}, Mg^{+2}, K^{+}, and Cl^{-}, HCO_3^{-}, SO_4^{-} and CO_3^{-2}. Waters of similar relative proportions of cations and anions had 'f' values which were very similar.

It was concluded that by taking account of the geology of a region or by characterizing a particular water, an approximation of the total dissolved salt content could be obtained based on a judicious choice of 'f' and providing the chemical composition of the TDS did not subsequently change. For example, waters draining limestone and dolomite beds are expected to contain bicarbonates of Ca^{+2} and Mg^{+2}. Based on the study results, waters high in carbonate have a low 'f' factor. The factor for natural waters of this type would necessarily be low.

Determination of total dissolved solids using specific gravity measurements has not been widely accepted. It has shown some promise in the dissolved solids determination of ground and surface waters exhibiting similar hydrochemical facies. Serious error would not be introduced unless the facies were to alter radically.

The method is quite simple and easy to use once the correct factor for a particular water type has been established. In most cases, this requires the development of a new factor for each type of natural water or for each waste stream at a plant by relating the specific gravity measured with the total dissolved solids.

3.2.6 Sum of Constituents Method. Another procedure commonly used in the determination of total dissolved solids consists of summing the concentrations which are determined separately for all the anions and cations in the water. This method is very useful because it not only gives the total dissolved solids, but an indication of the chemistry of the water as well (e.g., the ratios existing between the concentrations of the various solutes independent of the total dissolved solids). This method is also valuable because it allows identification of individual species which may be of significant concern environmentally and which may compose a large part of the total. This method also may give a more accurate indication of TDS for waters of a certain type than the evaporative method, for example, which might include water of crystallization. Although the method is theoretically a very good one, in practice it can be quite difficult to obtain analysis of all constituents required. This is likely the best method for unknown waters and a baseline method from which other methods may be developed.

The major dissolved solids present in natural waters have already been discussed. Excluding waters subject to appreciable contamination by unusual solutes and the waters of certain mineral springs, the major inorganic solutes of natural waters include the carbonates, bicarbonates, sulphates and chlorides of calcium, magnesium, sodium, potassium and silica. The latter is usually, but not invariably, in non-ionic form. Although other anions and cations may be present, they are usually not in significant concentrations in terms of their contribution by weight to the TDS value. If any are present in appreciable amounts, however, the procedure must include them or the calculated TDS will be low.

Using only the major constituents of natural water, the computed method of total dissolved solids determination involves finding the concentrations of these individual species and expressing them in a specified form prior to their addition. Procedures for determining the individual species are numerous and a thorough discussion of the methods available is presented in a variety of sources. Generally, chloride and sulphate, are determined by wet chemical procedures either gravimetrically by precipitation or by titration. Recently, ion chromatography has also become a useful tool in the measurement of these and other anions. Sodium and potassium are frequently measured using atomic absorption spectrometry as are calcium and magnesium. Calcium and magnesium which are sometimes termed "hardness" are more often determined by titration with the complexing agent ethylenediaminetetracetic acid (E.D.T.A.). Carbonate and bicarbonate are frequently termed the alkalinity of a sample and are usually measured by titration with a standard acid.

Once the various species have been determined, they are expressed in the form in which they were present in solution and added together to give the total dissolved solids. Frequently in developing standard procedures for computing the sum of dissolved constituents, the calculated total will be used either as a substitute for total dissolved solids determined as the residue upon evaporation or as a means of checking the result obtained by the evaporation method. It is necessary that all species determined for use in the computed method be expressed in the form they would have upon evaporation. An example of this is bicarbonates which are converted to carbonates during heating and evaporation. In this case, the desired result is an expression in terms of carbonate. This is achieved by multiplying the bicarbonate reported by a factor of 0.4917. Alternatively, if the alkalinity obtained is expressed as calcium carbonate, a factor of 0.6 is applied to express the result as carbonate. The carbonate figure is then used in the computation of the sum. In this way, the value obtained for total dissolved solids represents the dry

residue rather than the actual material in solution. The assumptions made to justify this expression of results as carbonate are:

1) that the conversion of bicarbonate to carbonate is quantitative; and
2) that the alkalinity measured is due only to bicarbonate and carbonate and not to the presence of OH^-.

The first condition is not necessarily true as explained earlier in the evaporative method. The second assumption is also not always correct but is not far from correct when applied to most natural waters.

An example of the use of this method is provided by Kemp (1971) who developed an equation for the dissolved solids of a water based on the major constituents which he regarded as carbonic, sulphuric and hydrochloric acids together with the hydroxides of calcium, magnesium, sodium and potassium. Expressing the major constituents in terms of their respective acids or bases in this way, he developed the expression:

$$T_S - 20 = 40\,(3c + 3m + n + p + s) + 5.5\,h \times 10^3$$

where
- T_S = total dissolved solids in mg/L
- c = molar concentration of calcium hydroxide ($Ca(OH)_2$)
- m = molar concentration of magnesium hydroxide ($Mg(OH)_2$)
- n = molar concentration of sodium hydroxide ($NaOH$)
- p = molar concentration of potassium hydroxide (KOH)
- s = molar concentration of sulphuric acid (H_2SO_4)
- h = molar concentration of hydrochloric acid (HCl)

This equation includes the contribution of silica to the total dissolved solids but does not make any reference to organic material. Kemp concludes that unless there are organic materials present which make a major contribution to the total dissolved solids, it is preferable to calculate the total dissolved solids from the analysis of the above constituents in the water sample.

The Inland Waters Directorate of Environment Canada used the standard W.Q.B. equations (Water Quality Branch, 1974):

(a) TDS Calc. = $Na + K + 0.393\ Ca + 0.243$ Total Hardness $+ Si + SO_4 + Cl + 0.6$ Total Alkalinity

(b) TDS Calc. = $Na + K + Ca + Mg + SO_4 + Cl + 0.6$ Total Alkalinity

in computing the total dissolved solids of waters taken from above and below a prairie reservoir (Allan and Richards, 1978). The data were from previous analyses of the water samples taken between 1960 and 1972. The value obtained using either equation was the same because the first equation can be reduced to the second equation.

Waters containing a residue on evaporation which includes water of crystallization have more reliable computed total dissolved solids concentrations. Generally, the computed dissolved solids of natural waters are more reliable than the determined residue on evaporation for concentrations above 1000 mg/L (Hem, 1959).

Before the computed dissolved solids method may be applied, all the major anions and cations present in the water must be determined. The component metals such as iron, boron or others must also be determined in waters which are unknown or likely to be influenced by industrial waste or sewage. As it is unreasonable in practice to include all species present in the water, the calculation of the computed dissolved solids will usually be slightly lower than the residue on evaporation. A difference of $\pm$ 10 to 20 percent can be anticipated as normal (Hem, 1959).

Errors in the values obtained for total dissolved solids using the calculated method are most notably associated with the exclusion of some species, as previously mentioned, and also with the individual errors inherent in the analytical determination of each species included in the equation. The error associated with the sum of the constituents will be the sum of the experimental errors. Another source of error may be in the inclusion of some elements whose state in solution is not known. For example, silica which has alkaline properties in some chemical states may be titrated in the alkalinity determination and reported in terms of equivalent bicarbonate. Such errors will usually be small.

3.3 Differences in Analytical Methods

Analytical results from the various methods used to quantify dissolved solids in water are not necessarily the same. The differences in analytical methods can best be illustrated by comparing results of different methods on sample water types.

3.3.1 Prairie Surface Water. Water quality data for the Battle River near Unwin, Saskatchewan for the period 1961 to 1975 are shown in Table 3. Unwin is near the Alberta border, approximately 140 kilometres northwest of Swift Current, Saskatchewan. These data were used to determine the dissolved solids by the specific conductance method, evaporative method and the sum of constituents method by both the W.Q.B. equation and by summing all of the constituents for which analyses were made. Each of the four

TABLE 3 WATER QUALITY DATA - Battle River near Unwin, Saskatchewan (Anon., 1977)

Parameter	Concentration
Specific Conductance (µS/cm)	740
pH (units)	9.0
Filterable Residue	606
Total Hardness	258
Total Alkalinity	333
Sodium*	108
Potassium*	8.1
Calcium*	67
Magnesium*	26.2
Carbonate°	1
Bicarbonate°	406
Chloride*	18
Sulphate*	132
Total Kjeldahl Nitrogen	1.2
Total Phosphorus	0.41
Reactive Silica	10.1
Boron*	0.25
Fluoride*	0.21
Aluminum*	0.08
Chromium+	0.12
Manganese*	0.05
Iron*	0.047
Cobalt+	0.002
Nickel+	0.005
Copper*	0.003
Zinc*	0.001
Arsenic*	0.002
Selenium*	0.005
Strontium+	0.47
Molybdenum+	0.05
Silver+	0.01
Cadmium+	0.001
Barium+	0.1
Mercury+	0.6
Lead*	0.003

Note: all concentrations expressed in mg/L except where noted

* dissolved
\+ extracted
° calculated

methods gives a different TDS concentration (Table 4). Using the specific conductance and assuming a factor of 0.65, which is an average value of the conversion factor as reported in the literature, a TDS concentration of 481 mg/L would be obtained. This underestimates the filterable residue method (considered to be the standard method) by about 25 percent and illustrates the importance of carefully selecting a conversion factor from specific conductance to concentration. The conversion factor is very site-specific.

TABLE 4 COMPARISON OF TDS CONCENTRATION BY ANALYTICAL METHOD FOR WESTERN CANADIAN SURFACE WATER

Analytical Method	TDS Concentration (mg/L)
Specific Conductance	481*
Filterable Residue	606
Sum of Constituents	
W.Q.B. Equation	559
Sum of all Constituents	573

* Based on an arbitrary conversion factor of 0.65 which is an average value of the factor from the literature.

The standard method, filterable residue, gave the highest result of the four methods, subject to the errors previously described. The sum of constituents method using the W.Q.B. equation gave a result which was 8 percent less than the filterable residue method. The sum of all constituents analyzed gave a greater TDS concentration than the W.Q.B. equation. The W.Q.B. equation is a simplified form of the sum of all the constituents analyzed method, however, in this case of a natural surface water, the simplification results in a small error of 3 percent.

3.3.2 Metal Cleaning Wastewater. The chemical analyses of a boiler fireside cleaning wastewater are shown in Table 5. Dissolved solids concentration as determined by specific conductance, filterable residue and sum of constituents by the W.Q.B. equation and of all analyzed constituents are summarized in Table 6.

Using a conversion factor of 0.65, the TDS concentration based on the specific conductance would be 2960 mg/L. This conversion factor is an average value from the literature for natural surface waters. In this case, a boiler washwater, the result is less than half the TDS concentration measured by the filterable residue method and further

TABLE 5 BOILER FIRESIDE WASH WATER (Tang et al., 1980)

Parameter	Concentration
Specific Conductance (μ S/cm)	4450
pH (units)	2.4
Filterable Residue	6100
Total Hardness	64
Total Alkalinity	0
Sodium	5.5
Potassium	0.1
Calcium	30
Magnesium	34
Carbonate	0
Bicarbonate	0
Chloride	71
Sulphate	6000
Total Kjeldahl Nitrogen	0.45
Total Phosphorus	0.2
Silica	100
Boron	0.32
Fluoride	-
Aluminum	7.4
Chromium	-
Manganese	15
Iron	1300
Cobalt	-
Nickel	55
Copper	8.6
Zinc	4.3
Arsenic	0.09
Selenium	0.008
Strontium	-
Molybdenum	-
Silver	0.01
Cadmium	0.001
Barium	7.9
Mercury	0.0002
Lead	0.01
Beryllium	0.01
Titanium	1.0
Vanadium	20

Note: - all concentration expressed in mg/L except where stated otherwise
- results based on characterization analysis of sample

TABLE 6 COMPARISON OF TDS CONCENTRATION BY ANALYTICAL METHOD FOR BOILER FIRESIDE WASH WATER

Analytical Method	TDS Concentration (mg/L)
Specific Conductance	2960*
Filterable Residue	6100
Sum of Constituents	
W.Q.B. Equation	6140
Sum of all Analyzed Constituents	7660

* Based on an arbitrary conversion factor of 0.65 which is an average value of the factor reported in the literature for natural suface waters.

illustrates the importance of selecting a conversion factor specific to the water being analyzed.

The result using the standard method of filterable residue gave a concentration of 6100 mg/L. It has been shown that the sum of constituents method for natural waters is more reliable for concentrations greater than 1000 mg/L (Hem, 1959). It is therefore likely that this is an underestimate of the true TDS concentration of the wastewater.

The W.Q.B. equation gave a result close to the filterable residue method; however, due to the low pH of the wastewater there is no alkalinity, and the equation only considers the presence of sodium, potassium, calcium, magnesium, sulphate and chloride. The presence of iron (1300 mg/L), nickel (55 mg/L), or other dissolved metals which may be present in industrial wastewaters in much higher concentrations than are normally found in natural surface waters are not considered using this simplified method.

The sum of all constituents gave the greatest result which was about 25 percent greater than that obtained by the filterable residue method. Due to the relatively high TDS concentration (greater than 1000 mg/L) this method probably gives a result closest to the true TDS concentrations of the wastewater in this case.

3.3.3 Comparison Between Specific Conductance and TDS for Two Wastewaters. The relationship between specific conductance and dissolved solids for two wastewaters; FGD waste leachate from an eastern U.S. plant and a combined ash lagoon water from a western Canadian generating station is compared in Figure 9. Both wastewaters contain proportionally high concentrations of sulphate, calcium, magnesium, and sodium but each

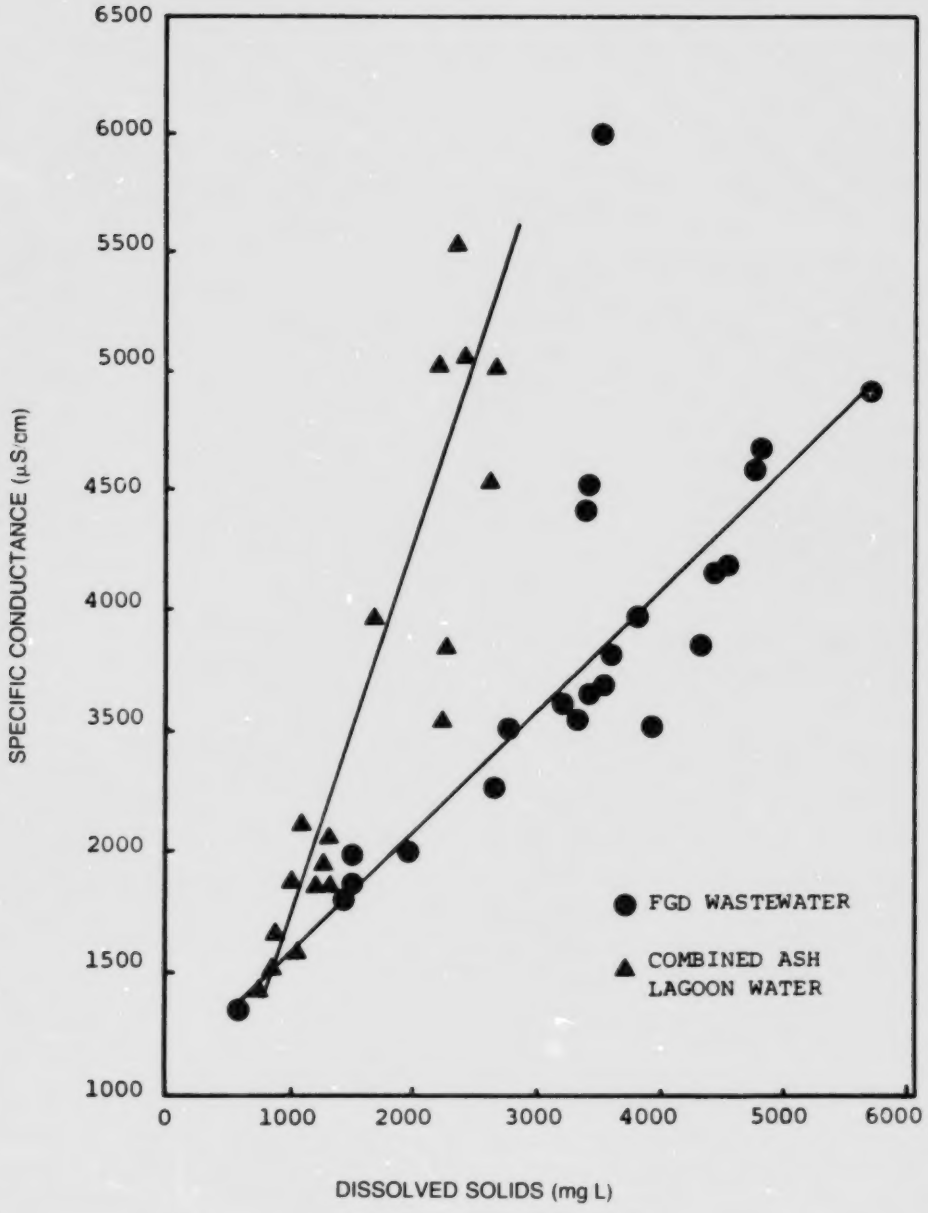


FIGURE 9 RELATIONSHIP BETWEEN SPECIFIC CONDUCTIVITY AND DISSOLVED SOLIDS FOR TWO WASTEWATERS

has a very different conductivity to TDS relationship as shown by the slopes of the lines. For example, a specific conductivity of 5000 μS/cm would be equivalent to 2400 mg/L TDS for the combined ash lagoon water and 5800 mg/L TDS for the FGD sludge leachate. In general, waters containing mostly bicarbonates or chlorides tend to give a lower TDS by calculation than by the conductivity method. Sulphate containing waters, particularly those affected by solution of gypsum and highly silicious waters, tend to be over-estimated when the TDS is calculated from a conductivity measurement (Hem, 1959). This illustrates that although the wastewater may have similar specific conductivity and linear relationships and may be composed of proportionally similar chemical constituents, other factors may be sufficiently significant to greatly affect the conductivity versus dissolved solids relationship. The relationship of TDS to conductance becomes indefinite for waters very high in dissolved solids (over 30 000 mg/L) (Hem, 1959).

3.4 Summary

Water contains impurities in a variety of forms. Dissolved solids compose part of these impurities and include inorganic ions and molecules as well as small organic molecules and colloids. Different definitions of dissolved solids are often arbitrary and based on a particular method of analysis. Often the dissolved solids present or as reported in an analysis differ greatly from the commonly understood idea of what dissolved solids are. This is particularly true for the results of analytical determinations of dissolved solids for some industrial wastewaters in comparison to natural waters.

Natural waters in areas remote from industry or municipal discharges contain for the most part a small number of major ionic species. The ions Ca^{+2}, Mg^{+2}, Na^{+}, HCO_3^{-}, Cl^{-} and SO_4^{-2} are the main constituents of dissolved solids in these waters. In some situations, silica may also be important. In contrast, the constituents of industrial wastewaters may vary considerably from this.

Five different analytical procedures have been described for the determination of dissolved solids in water. These are dissolved solids by; evaporation (gravimetric), conductivity, refractive index, density, and summation. Each method has its relative advantages and disadvantages. Values of total dissolved solids obtained by each method include values of different parameters and hence the definition of TDS changes depending on the procedure used.

The evaporative procedure is the most common and is widely accepted as the standard procedure for determination of TDS in water and wastewater. Results obtained using this procedure are termed residue on evaporation or filterable residue. The method is subject to some error and ambiguity since the residue on evaporation does not

completely represent the material originally present in the solution. For example, bicarbonate (HCO^-_3) which may be present in solution will be converted to carbonate (CO_3^-) during the evaporation under heat with the loss of carbon dioxide (CO_2) and water (H_2O). Also, salts which may exist in hydrated form in solution may lose their water of hydration upon crystallization. The evaporative method is the usual procedure to which all other analytical methods are compared and does not require assumptions of the species composition or relationships between chemical species composing the TDS.

Another procedure which is widely used for dissolved solids determinations is by conductivity measurements. The conductivity of a solution of electrolytes can be correlated with the concentration of ions present. Linear curves obtained by regression analysis can then be used to obtain total dissolved solids once the conductivity is known. This method is limited because a different calibration curve must be prepared for different characteristic types of water as conductivity depends on the species of salts present. Also, the method is limited to solutions of electrolytes. Organic compounds which do not dissociate in water and therefore are not good conductors, will not be measured.

Refractive index measurements have been used to determine dissolved solids. This technique is based on the change of the speed of light in an optically denser medium than air. The dissolved solids determined using this procedure include organics and inorganics. The method requires a specific curve correlating relative indices of refraction and dissolved solids for each different type of water as is necessary with the conductivity procedure. Measurements made using refractometers are very fine and require a high degree of precision. Hence, this may be an impractical analytical technique where good laboratory conditions are not available.

Total dissolved solids have also been determined by specific gravity. The method involves measuring specific gravity and relating it with the concentration of dissolved solids as determined by evaporation. The relationship between total dissolved solids and specific gravity can be quite complicated. Again, a specific correlation curve for each different type of water must be prepared as factors will differ for different waters. Waters of similar hydrochemical facies have similar correlation coefficients.

Procedures for determination of total dissolved solids by summation of the individual constituents are available. Waters must first be characterized to determine the main constituents. Since the main constituents of natural waters are comprised of the cations Ca^{+2}, Mg^{+2}, and Na^+ and the anions Cl^-, SO_4^{-2} and HCO_3^-, the number of species needed in the summation is relatively few. Industrial wastewaters, however, may contain

many dissolved solids species which would require an extensive characterization to identify them. In either application, the concentrations of each of the constituents are determined independently and then added together to give the total dissolved solids.

The summation method can be quite time consuming and requires either prior knowledge of the chemical species present in the water or an extensive characterization. A more complete picture of the dissolved solids content is, however, obtained and in some cases may be more accurate than the total dissolved solids determination by evaporation.

Dissolved solids in water are subject to considerable misconceptions. One unit of TDS as determined using one procedure does not necessarily equal another unit determined by a different procedure. Different methods of analysis may give different results. The procedure used, therefore, must always be specified when stating TDS values. The assumptions behind the choice of the procedure should be provided as well. This is particularly important when considering industrial wastewater which may be more complex and varied in terms of the chemical constituents composing the TDS.

4 COAL-FUELLED STEAM ELECTRIC GENERATING STATIONS

4.1 Introduction

The electric power generation industry in Canada is technologically and geographically diverse. Existing plants have a broad range of generating capacities, station designs and site-specific operating conditions. In addition, generating stations across Canada operate under a variety of climatic conditions.

Surface waters available for use by generating stations vary widely in quality and this is often reflected in the design of the system. Treatment plant design for instance varies considerably depending on the characteristics of the raw water supply. As a result, the nature of the wastewaters from the plant also vary in composition and concentrations.

Several new pollution control technologies may also contribute to the concentration and change of dissolved solids contents in wastewaters from coal-fired generating stations. Flue gas desulphurization systems, for example, may have wastewater streams which can significantly increase the magnitude of dissolved solids discharges. Again, the composition of these wastestreams depends on the coal composition, scrubber design and system operation.

Total dissolved solids are particularly significant as a pollutant in discharges from stations where closed loop systems are used to recirculate or reuse wastewaters. These systems tend to concentrate dissolved solids due to evaporation and may require periodic blowdown to maintain TDS concentrations within ranges dictated by process equipment. The blowdown from such systems may contain "natural" TDS concentrations which are detrimental to the environment.

No one existing or planned station would illustrate all of the potential problems of dissolved solids. There is a wide variability in site-specific operating factors. Existing Canadian generating stations have limited operating experience with new technologies such as near zero discharge water management schemes or flue gas desulphurization systems. For this reason, the approach of using generating station models was selected to address the potential problems of dissolved solids discharges from Canadian steam electric stations. These models were developed to include regional operating factors and new pollution control technologies. This approach results in a first approximation to the characteristics and variability of dissolved solids discharges to be made. Based on this, applicable treatment technologies for the removal of dissolved

solids can be reviewed and the operating problems and costs associated with these technologies identified.

Two generic steam electric generation station models have been developed to identify the characteristics of wastewater streams in terms of total dissolved solids. One of these represents conditions and new station configurations in Eastern Canada. The other model represents a Western Canadian situation.

Models for this type of study are useful since questions associated with the discharge of dissolved solids from Canadian steam electric stations are only beginning to be addressed. On-site characterization studies of wastewaters at all existing stations have not yet been completed and a comprehensive data base does not yet exist. As well, new technologies which will be incorporated into planned steam electric generating stations are known to produce effluents which contain high concentrations of dissolved solids. However, some of these technologies are not yet in operation in Canada. Consequently, as a starting point, models assist in identifying both present and future problems to help focus on future research efforts.

Each generating station model is accompanied by a flow and chemical characterization of major wastewater streams. The analyses shown allow the total dissolved solids to be calculated using the Inland Waters Directorate standard equation which is designated by the abbreviation $TDS_{(a)}$ (Allan and Richards, 1978). $TDS_{(e)}$ designates concentrations determined using the evaporative method. The results of the two analytical methods can be compared and typical metal concentrations in the wastewaters are shown. Trace metals such as aluminum, arsenic, barium, beryllium, boron, cadmium, chromium, cobalt, copper, lead, lithium, manganese, mercury, molybdenum, nickel, selenium, silver, strontium, thorium, titanium, vanadium, zinc and zirconium may be found. Additional metals have been listed because currently they are of particular interest from an environmental perspective. Other metals may also be present in concentrations equal to or greater than the concentrations of some of the trace metals shown here. In addition to the flowrate, the chemical characteristics are used in the evaluation and selection of appropriate control technologies.

4.2 Eastern Station Model

The station model of an Eastern Canadian steam electric generating station is shown in Figure 10. The characteristics of the station are:

- 400 MW generating capacity,
- high sulphur bituminous coal fuel,

PARAMETER	AIR PREHEATER WASH	BOILER FIRESIDE WASH	BOILER STEAMSIDE WASH	COAL PILE RUNOFF	FILTER BACKWASH	ION EXCHANGE REGENERANTS		FLY/BOTTOM ASH DISPOSAL SITE RUNOFF/LEACHATE	BOTTOM ASH SYSTEM BLOWDOWN	BOILER ROOM SUMP	CONDENSATE POLISHER REGENERANT	ONCE-THROUGH COOLING WATER	FGD SLUDGE DISPOSAL SITE RUNOFF/LEACHATE	FGD SYSTEM BLOWDOWN
						CATION	ANION							
FLOW	500 000 L	1 000 000 L	600 000 L	0.6 L/s	0.9 L/s	1.3 L/s		1.5 L/s	23 L/s	20 L/s	0.4 L/s	17 000 L/s	1.5 L/s	11 L/s
MODE	PERIODIC	PERIODIC	PERIODIC	CONTINUOUS	CONTINUOUS	CONTINUOUS		CONTINUOUS	CONTINUOUS	CONTINUOUS	CONTINUOUS	CONTINUOUS	CONTINUOUS	CONTINUOUS
pH (units)	2.5	2.7	9.2	2.2	7.0	1.0	13.1	7.1	7.2	11.8	2.8	7.7	7.8	12.0
CONDUCTIVITY (µS/cm)	12 000	5 300		10 800	180	97 000	100 000	1 600	2 500	2 900	800	60 000	3 300	11 000
TDS (a)	37 000	6 200	58 500	28 400	136	12 300	18 200	1 410	1 820	1 600	28	25 000	3 440	15 000
TDS (e)	28 700	2 530		13 800	99.6	1 466	37 600	1 400	1 470	1 670	75.5	25 300		
IRON	7 560	1 080	6 900	5 320	0.7	0.3	6.2	0.7	23	13	0.2	1.1	0.4	1.0
OTHER METALS	1 330	936	1 000	610	5.2	7.1	0.5	17	20	50	<0.1	7.5	35	14.0
CO_3	0	0		0	0	0	3 000	1.5	0	103	0	0		
HCO_3	0	0	0	0	61	0	0	170	152	6.4	0	110		
SO_4	27 660	1 280		13 000	20.8	180	20 300	840	860	740	73	1 780	1 740	770
PO_4	157	62	75	1 000	0.1	0.1	0.2	2.0	5.6	6.3	<0.1	0.2	<1	2.0
Cl	14	30		48	9.6	150	45	40	13	14.3	0.4	14 900	280	2 830
Ca	513	703	45	445	30	665	0.5	330	410	58	0.1	280	560	2 900
Mg	48.6	18.6	11	122	2.2	110	0.1	8.0	3.0	4.4	<0.1	890	150	538
Na	58	176	370	139	7.0	154	4 570	70	74	530	2.0	7 080	31	185
K	204	344		<3	<1	7	2	31	14	30	<1	300	0.8	40

NOTE: All values in mg/L unless otherwise indicated.
(a) — Sum of constituents method.
(e) — Evaporative method

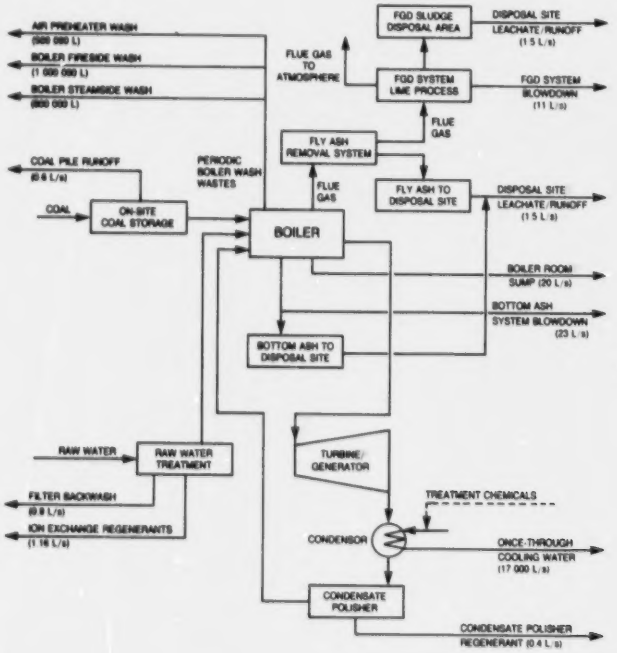


FIGURE 10 EASTERN CANADIAN GENERATING STATION MODEL

- dry fly ash handling system,
- recirculating bottom ash handling system,
- once-through seawater cooling,
- limestone based flue gas desulphurization system,
- combined fly and bottom ash disposal area, and
- separate flue gas desulphurization sludge disposal area.

The operation of a generating station with these characteristics would produce 13 major wastewaters; 10 more or less continuously and 3 periodically.

4.2.1 Periodic Wastewaters. Wastewaters which are usually described as periodic include those produced during equipment cleaning such as air preheater, boiler fireside, boiler steamside and other metal surface cleaning and treatment wastestreams. In addition to the removed substances, these wastewaters may also contain residues of any specialty cleaning, anti-corrosion or metal surface conditioning chemicals which were used in the cleaning and/or treatment sequence.

The buildup of combustion waste deposits on the air preheater heat transfer surfaces may significantly reduce their heat transfer efficiency. In coal-fuelled stations, deposits are primarily fly ash like solids. Typically, the air preheaters are cleaned during each station shutdown, but they may require cleaning more frequently than the annual shutdown permits. New air preheater designs are being developed which permit on-line cleanings as frequently as several times per month. The wastewater volume of 5.0×10^5 L shown in the Eastern Station Model (Figure 10) is based on a single cleaning with only a high pressure water spray without specialty chemical additives for cleaning or metal treatment. The wastewater chemistry is based on the analysis of a limited number of samples and is consistent with other characterizations reported in the literature as well as what would be anticipated from eastern Canadian coal residues.

The charateristics of this wastewater are considerably different from those of natural surface waters. The 2.5 pH is substantially below the normally encountered range in natural waters. The iron concentration of 7560 mg/L and the "other metals" concentration of 1320 mg/L are similarly abnormal. The high "other metals" concentration suggests that several of the trace metals constituents are present in toxic concentrations and amounts to roughly one quarter of the $TDS_{(e)}$ content. The $TDS_{(e)}$ level is comparable to seawater but the balance of contributing dissolved species is not similar. With the exception of sulphate which accounts for roughly three quarters of the

$TDS_{(e)}$ contents, the contributions of the naturally occurring major ions account for a small fraction of the $TDS_{(e)}$.

There is substantial disagreement between the $TDS_{(e)}$ value (37 000 mg/L) and the $TDS_{(a)}$ value (28 100 mg/L). It might be difficult to develop a suitable "f" factor for an accurate TDS measurement by conductance for this particular wastewater type especially if sequential washings and rinsings involving specialty chemicals were involved. Neither an accurate TDS measurement nor a TDS measurement plus the measurement of the parameters shown in this example would provide an adequate basis for a judgement of the safety of this wastewater. Elevated trace toxic metals concentrations are probably involved and if specialty chemicals were utilized some unusual organo-metallic might be of concern as well.

Boiler fireside cleaning is carried out for the same reasons which make air preheater washing necessary. Deposits from combustion residues also inhibit detailed boiler inspections. Like air preheater cleaning, boiler fireside cleaning has traditionally been carried out during major station shutdowns. In the simplest type of cleaning, high pressure water is used to remove deposits and the volume of wastewater produced is dependent on a combination of the pressure and amount of water required. For this model a simple single cleaning without specialty chemical additives, which produces 1×10^6 L of wastewater, is used. The wastewater chemistry, based on a limited number of samples, shows a $TDS_{(e)}$ concentration of 6200 mg/L. While this TDS value is considerably less than the air preheater wastewater, it is still high by comparison to natural inland surface waters. The major constituents of the TDS are again sulphates, iron and other metals, although the iron and 'other metal' fractions are proportionately higher than the sulphate fraction but lower than in the air preheater wastewater.

As was the case with air preheater wash, the boiler fireside wash contained high TDS concentrations primarily composed of dissolved metals. Because of the low pH and the presence of the TDS which are not naturally occurring, the TDS is not a meaningful parameter to safely describe this TDS characteristics of this wastewater.

No published data are currently available on the volume of wastewater produced or the chemical characteristics of a boiler waterside cleaning at an eastern Canadian steam electric station. The volume of wastewater estimate is based on the equation:

$$\text{boiler volume} = 1763\ (MW)^{0.79}$$

where MW is the generating capacity of a drum type boiler (Goldstein et al., 1980).

It is assumed that three boiler volumes of wastewater would be generated. This equation likely over-estimates the volume for supercritical units. The wastewater chemistries are those developed by the U.S. EPA (Castle, 1980). High levels of $TDS_{(e)}$ would be expected since large volumes of strong acids, usually hydrochloric acid, are used during the clearing procedure.

The constituents of the TDS such as chlorides are found in naturally occurring waters, however, the balance between the constituents which occurs in natural water is not maintained and unusual ionic forms as well as complexed or chelated organo-metallic forms may be present depending on the cleaning solution employed. For these reasons, TDS content alone will not adequately describe this wastewater.

4.2.2 Continuous Wastewaters. Continuous wastewaters are those which are produced during the day to day operations of a coal-fired generating station. These include condenser cooling water, wastewaters resulting from the preparation of water for the steam cycle and blowdowns from ash transport systems and flue gas desulphurization systems. Other wastewaters which are produced on a frequency depending on climatic conditions such as coal pile and ash disposal area runoff are also included in this group.

Coal pile runoff results from the contact of precipitation with high sulphur coal stored on-site at the generating station. It has been chemically characterized for eastern Canadian situations (Dearborn Env. Cons. Ser., 1982). The volume of the wastewater produced depends on the shape and management of the coal pile. The flowrate of 0.6 L/s is based on flowrates observed during the summer at an eastern Canadian station. Analyses of samples indicates that this wastewater contains high $TDS_{(e)}$ concentrations which are composed primarily of iron, sulphate and phosphate.

The low pH and high dissolved metals content of coal pile runoff significantly affects the ionic composition of the TDS. For this reason, the TDS composition in this wastewater is not similar to that occurring in most natural surface waters.

During the preparation of water for use in the steam cycle, sand and carbon filters are used to remove suspended solids and organics following clarification. These filters are backwashed periodically using clear, well water which produces a wastewater. The frequency of the filter washing is determined by the efficiency of the clarification step and the demand for water in the station. On-site studies indicate that about 0.9 L/s of this wastewater would be produced. Analyses of representative samples indicates that relatively low $TDS_{(e)}$ concentrations are present. The TDS are primarily composed of

calcium, chloride and sulphate and the calculated TDS and the evaporative procedure TDS results are very similar. The pH, chemical constituents and constituents balance in this wastewater are similar to those in natural waters. For this reason TDS could be used as a meaningful descriptive parameter here.

Water that is being prepared for the steam cycle passes through an ion exchange system consisting of both cationic and anionic exchange resin beds. The ion exchange process can be designed to remove all mineral salts using bead form organic resins. The beads attract chemical ions of opposite charge, however, once all sites on the beds are exhausted, the resin must be regenerated. The resulting ion exchange wastes are either strongly acidic or alkaline and contain high concentrations of dissolved salts.

Based on flow monitoring and sample analysis, a combined flow of 1.3 L/s of regenerants would be expected. The cationic bed regenerants would be highly acidic with high $TDS_{(e)}$ composed of calcium, magnesium, sodium, chloride and sulphate. The anionic bed regenerants are very alkaline with high $TDS_{(e)}$ composed of sulphate, sodium and carbonate.

Although the major components of the TDS in these wastewaters are similar to those of natural waters, the balance between the constituents may not be maintained. The pH values are extreme and toxic forms of dissolved metals could be present as a result. Because of this, the TDS value alone does not describe this wastewater adequately.

4.2.3 Boiler Room Sump. Small water spills and miscellaneous wastewaters are usually collected in a floor drain system of the boiler house. This wastewater along with wastewaters from the boiler room areas are usually combined in the boiler room sump. This sump, therefore, can contain a wide variety of wastewaters which have very different characteristics. For the 400 MW generic station flows of 20 L/s could be possible. Analyses of samples collected at Eastern Canadian generating stations indicate $TDS_{(e)}$ concentrations of 1600 mg/L which are primarily composed of sodium, calcium, sulphate and carbonate.

For this wastewater, there is good comparison between the calculated TDS and the results from evaporative procedure, however, the high pH may change the chemical species, particularly of metals in comparison to natural surface waters. The TDS of this wastewater, therefore, cannot be relied upon to be directly comparable to that of natural waters.

4.2.4 Polished Regenerants. The condensate polisher is composed of a mixed bed of cationic and anionic ion exchange resin beds. It is used to maintain the high quality of returning condensate to the boiler. As with the ion exchange resin in the raw water treatment plant, these resin beds must also be regenerated periodically.

Results of an on-site sampling and analytical program show that a low flow would be typical. The $TDS_{(e)}$ would be low, composed primarily of sulphate.

The difference between the evaporative and calculated TDS concentrations is probably related to the low pH which affects the carbonate/bicarbonate equilibrium. The TDS of this wastewater is not comparable to that of natural water for this reason.

4.2.5 Bottom Ash System Blowdown. The generic model representing eastern Canadian conditions contains a recirculating hydrobin type bottom ash system. Although these systems can theoretically operate without a blowdown, in reality a blowdown is often required. This is necessary because of unintentional make-up through ash pump seal water supplies and cascade water use schemes where other wastewaters in the plant are routed to the ash system. Based on measurements and the analysis of samples from an operating system of this type in Eastern Canada, a flowrate of 23 L/s would be expected with a $TDS_{(e)}$ of about 1800 mg/L composed primarily of sulphates and calcium.

The near neutral pH and similar TDS concentrations obtained from the sum of constituents and evaporative procedures would suggest that the TDS could be used to describe this wastewater. However, this water was in contact with ash and was likely contaminated with concentrations of trace metals not normally found in natural waters at these levels. For this reason, direct comparison of these TDS values and those from natural waters cannot be made for environmental protection purposes.

4.2.6 Flue Gas Desulphurization System Blowdown. There are no operating FGD systems in Canada at steam electric generating stations yet. The nature of the high sulphur coals used in Eastern Canada would suggest the use of either a lime, limestone or Wellman-Lord FGD system. The generic model uses a limestone based system and although such systems can theoretically operate without a blowdown, experience at operating systems in the U.S. indicates that blowdown from the system will likely occur. Based on a recent study and adjusting for the high sulphur content of the coal, a blowdown of about 11 L/s is possible (Env. Canada, 1980). Based on the analyses of samples from similar systems in the United States, this wastewater would likely have high $TDS_{(e)}$ of about 1.5×10^4 mg/L which consists primarily of chloride, calcium, sulphate and magnesium.

The extremely high TDS concentration present in this wastewater is present at a relatively high pH, therefore, direct comparison cannot be made with natural waters.

4.2.7 Once-through Cooling Water. The generic model for Eastern Canada utilizes a once-through seawater condenser cooling system. The flowrate is based on estimates of the cooling water requirement for the model station while the chemical characteristics are those of seawater. The only change with respect to the chemistry would be the likely addition of chemicals used for corrosion control in the condenser. Typically, 35 mg/L of ferrous sulphate is used for this purpose which increases the concentration or iron and sulphate in the condenser cooling water outfall.

4.2.8 Fly/Bottom Ash Disposal Area Runoff. When precipitation comes in contact with fly and bottom ash at a disposal site, a contaminated runoff results. The flowrate of the runoff is dependent on the disposal area topography and its management, while the chemical characteristics are related to the composition of the ashes.

Based on flow measurements and sampling programs at existing ash disposal areas a flow of 1.5 L/s could be expected at the generic station. The wastewater would likely have a $TDS_{(e)}$ of 1400 mg/L which is composed of bicarbonate, sulphate and calcium. This wastewater has a neutral pH and there is a good correlation between the calculated TDS and that determined using the evaporative procedure. However, it is likely that trace metals would be present in this wastewater in concentrations which are not normally found in natural waters and as a result, the TDS concentrations cannot be assumed to be the same as those of natural waters for environmental protection purposes.

4.2.9 FGD Sludge Disposal Site Runoff. There are no FGD disposal sites in Canada at this time. Based on the assumption that similar conditions in terms of sludge disposal site configuration, management and runoff coefficients would exist at FGD sludge disposal and ash disposal areas, the wastewater flowrates are assumed to be the same. The characteristics of the wastewater are based on analyses of samples of runoff from stations in the United States with similar FGD systems and operating characteristics. The $TDS_{(e)}$ would be about 3400 mg/L and would be composed of primarily sulphate, chloride, calcium and magnesium.

The balance between the constituents of the TDS as measured by the evaporative procedure in this wastewater is probably not comparable to that of natural waters due to the relatively high sulphate concentrations in comparison to the other cationic species.

4.3 Western Station Model

The station model of a western Canadian steam electric generating station and representative wastewater chemistries and flows are shown in Figure 11. The characteristics of the station are:

- 400 MW generating capacity,
- low sulphur lignite coal fuel,
- combined fly and bottom ash transport with lagoon disposal,
- recirculating cooling tower, and
- no flue gas desulphurization.

The operation of a generating station with these characteristics would produce ten major wastewaters: three periodic and seven continuous. Much less is known about the wastewater characteristics and flowrates of these wastewaters in a western Canadian situation. The approach used to develop typical flowrates and wastewater chemistries for the western generic model was the same as that used for the eastern model. It is appreciated that this approach may not produce conditions fully representative of those in Western Canada.

Discussion of the total dissolved solids concentrations has been limited to those wastewaters where chemical characterization data are available.

4.3.1 Periodic Wastewaters. No data are available on the flowrates or chemistries of periodic wastewaters at western Canadian steam electric generating stations. The flow data for each of the air preheater, boiler fireside and boiler waterside washes are based on data from western U.S. generating stations (Goldstein et al., 1980). Chemical characterization of these wastewaters has not been completed for western U.S. stations.

4.3.2 Continuous Flow Wastewaters. Runoff from lignite coal piles is not comparable to that from eastern Canadian coals due to the significant difference in sulphur content of the fuel. The runoff flowrate is based on estimates from a western generating station during summer conditions. Results of chemical analyses of samples of lignite pile runoff show that $TDS_{(e)}$ is about 800 mg/L with bicarbonate, sulphate, magnesium and sodium being the primary constituents.

The coal pile runoff, although nearly neutral, contains a relatively large proportion of dissolved metals which are not likely to be present in natural waters. As a

PARAMETER	AIR PREHEATER WASH	BOILER FIRESIDE WASH	BOILER STEAMSIDE WASH	COAL PILE RUNOFF	FILTER BACKWASH	ION EXCHANGE REGENERANTS		COMBINED ASH LAGOON OVERFLOW	BOILER ROOM SUMP	CONDENSATE POLISHER REGENERANT	REVERSE OSMOSIS REJECT BRINE	COOLING TOWER BLOWDOWN
						CATION	ANION					
FLOW	730 000 L	600 000 L	500 000 L	0.3 L/s	0.9 L/s	3.4 L/s		30 L/s	20 L/s	0.4 L/s	1.5 L/s	100 L/s
MODE	PERIODIC	PERIODIC	PERIODIC	CONTINUOUS	CONTINUOUS	CONTINUOUS		CONTINUOUS	CONTINUOUS	CONTINUOUS	CONTINUOUS	CONTINUOUS
pH (units)				7.5	7.0	1.0	13.1	9.8	9.4	2.8	6.3	7.0
CONDUCTIVITY (μS/cm)				4 300	180	9 700	100 000	1 800	1 950	600		
TDS (a)				3 270	136	123 000	18 250	1 200	1 750	28	28 000	11 000
TDS (e)					99.6	1 468	37 600		1 810	75.5		
IRON				530	0.7	0.3	0.2	0.4	1.8	0.2		5
OTHER METALS				1 670	5.2	7.1	0.5	15		0.1		40
CO_3				0	0	0	3 000	30	22	0		0
HCO_3				1 980	61	0	0	126	170	0	70	35
SO_4				2 100	20.8	180	28 300	5 790	910	73	19 000	5 800
PO_4				45	0.1	0.1	0.2	1.3	1.16	0.1		
Cl				28	9.6	150	45	18	27	0.4	800	1 200
Ca				850	30	865	0.5	58	400	0.1	190	1 000
Mg				330	2.2	110	0.1	38	83	0.1	900	1 500
Na				1 300	7.0	154	4 570	235	275	2.0	7 750	1 410
K				390	1	7	2	22	25	1		

NOTE: All values in mg/L unless otherwise indicated.
(a) — Sum of constituents method.
(e) — Evaporative method

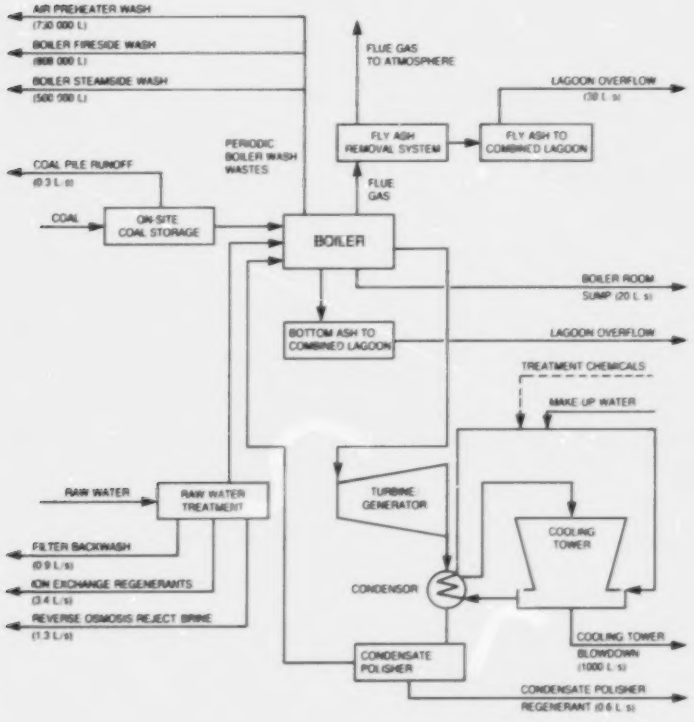


FIGURE 11 WESTERN CANADIAN GENERATING STATION MODEL

result, comparison cannot be made between the TDS concentration of this wastewater and that of natural waters.

Both sand and carbon filters would follow the clarification step in the preparation of raw water for use in the steam cycle. In the absence of analytical and flow data it was assumed that the chemical and flow characteristics would be the same as those from the eastern model.

Following filtration, raw water passes through ion exchange resins during its preparation for the steam cycle. The amount of salts which must be removed from the water is a function of the raw make-up water quality. Basically, the same exchange resins would be used in the western situation with the same removal capacity per unit volume of resin. It has been assumed that the cationic and anionic regenerants would be chemically similar to those at the eastern site, however, the volume has been increased to reflect the greater hardness of make-up water.

The design of the water treatment plant must take into consideration the chemical characteristics of the raw water supply. As new generating stations are built in areas where raw water quality is lower, more advanced technologies such as reverse osmosis will be required in the water treatment plant. The RO process produces a wastewater known as reverse osmosis rejects. It is anticipated that this wastewater would have a high $TDS_{(e)}$ concentration of about 1850 mg/L primarily composed of sulphate, magnesium and calcium. Based on a rejection rate of 85 percent of water flow through the system, the rejects would have a flow of about 1.5 L/S. This wastewater flow rate does not include other wastewaters associated with the maintenance of the RO system such as backwashing or flushing waters.

The TDS concentration of this wastewater cannot be directly compared to that of natural waters primarily because the balance between constituents of the TDS, and particularly for sulphate, has not been maintained. This balance in the wastewater is upset by the chemical treatment of the feedwater to the reverse osmosis system.

As with the eastern model, the polisher serves to maintain the high quality of the condensate which is returned to the boiler. In the absence of analytical data, the chemical characteristics and flowrate have been assumed to be the same as that for the eastern site.

4.3.4 Combined Ash Lagoon Overflow. In the western generating station model, both fly and bottom ash are hydraulically transported to a common lagoon for permanent disposal with the supernatant water recycled for further sluicing. Repeated ash to water contact may eventually increase concentrations of many chemical constituents and may

necessitate a blowdown from the system. Alternatively, suboptimal water management practices may result in the accumulation of greater volumes of water in the ash system when other wastewaters are disposed of in the ash lagoon. A blowdown may be necessary to maintain the design water balance or to prevent the build-up of chemical constituents which may cause operating problems such as the formation of scale. Analyses of samples from combined lagoons in Western Canada indicate that $TDS_{(e)}$ of 1500 mg/L primarily composed of sulphate, sodium, and bicarbonate can be expected.

Although the pH of this wastewater is relatively high, the main reason that it cannot be compared to the TDS of natural waters is that it contains low concentrations of many contaminants as a result of contact with the ash. These trace contaminant levels would not normally be found in natural waters simultaneously.

4.3.5 Boiler Room Sump. The boiler room sump is usually the collection facility for a variety of miscellaneous wastewaters such as floor drains, stream trap drains and other spills or losses. It has been assumed that the flow which reflects both station design and housekeeping practice would be the same as the eastern generating station. Analyses of samples collected from a representative site in Western Canada contained about 1700 mg/L $TDS_{(e)}$ with the main constituents being sodium, sulphate and bicarbonate.

4.3.6 Cooling Tower Blowdown. Currently one station in Western Canada utilizes a cooling tower for primary condenser water cooling, although a second station uses a tower for auxiliary cooling in the summer. It is anticipated that, as cooling water supplies become less available, cooling towers will become more prominent in the industry particularly in Western Canada.

Blowdown water is regularly withdrawn from the recirculating water to control the buildup of suspended and dissolved contaminants in the system and may contain biocides, chromates (corrosion inhibitors) and highly dissolved solids. Typically, cooling tower blowdown represents about 10 percent of the evaporation losses (Probstein and Gold, 1978; Wat. Pur. Assoc., 1976). Using the U.S. DOE procedure (1981) and cooling tower operating conditions from the Great Plains area, about 1030 L/s of blowdown could be anticipated. High $TDS_{(e)}$ concentrations of 11 000 mg/L primarily composed of sulphate, chloride, calcium, magnesium and sodium can be expected.

The cooling tower blowdown contains the same dissolved solids as the natural makeup water. The balance between the constituents is probably not changed in the wastewater compared to natural waters unless some softening process has taken place. The blowdown may, however, contain low concentrations of chemicals used for scale and

biological growth inhibition if they have been used. Comparison between the TDS concentration in the blowdown and that of natural waters can only be made with consideration of these two conditions.

4.4 Summary

The approach of using model generating stations to identify specific concerns has limitations when very detailed information is desired. It is very useful, however, in the identification of major differences and trends. The TDS concentrations which have been determined by several analytical methods for wastewaters from an eastern and western Canadian model generating station are summarized and compared in Table 7.

The $TDS_{(e)}$ concentration of most of the major wastewaters exceeded the levels typically found in Canadian surface waters. The exception to these were the filter backwash and condensate polisher regenerants. For some wastewaters such as the periodic wastewaters, the TDS concentrations were one hundred times greater than concentrations occurring naturally in the arid regions of western Canada.

Agreement between TDS concentrations determined by the evaporative and sum of constituents methods appears to depend on the nature of the wastewater. For example, good agreement was observed between boiler room sump waters, ash disposal site runoff, ash lagoon overflow and reverse osmosis rejects. In the first three cases, there is extended contact time between the source of dissolved species (suspended solids) and the wastewater, permitting chemical equilibria to be at least partially established. In the case of R/O rejects, the dissolved species present are those removed from the natural surface feed water by the process. Although the concentration of these may be greater than in the raw water, the ratios between the main constituents remain relatively similar.

In contrast, periodic washwaters from the air preheaters, coal pile runoff at the eastern site and ion exchange regenerants do not show good agreement between $TDS_{(e)}$ and $TDS_{(a)}$ values. In the first two cases, the water is in contact with relatively highly soluble solids (fly ash type solids and in the second case high sulphur coal) which results in high concentrations of dissolved metal species. This in turn produces higher TDS concentrations than normally found in natural water which are composed of very different components. In the case of ion exchange regenerants, the process requires the addition of large amounts of either very acidic or very alkaline chemicals. This results in wastewaters with TDS concentrations much greater than and different in composition from those found in natural surface waters.

TABLE 7 COMPARISON OF TDS BY SEVERAL METHODS FOR POWER STATION WASTEWATERS

Region	Wastewater	$TDS_{(e)}$	$TDS_{(a)}$	Conductivity S/cm	Apparent "f" Factor*	Comment
Eastern	air preheater wash	37 000	28 700	12 000	3.08	low pH, dissolved trace metals
	boiler fireside wash	6 200	2 530	5 300	1.17	low pH, dissolved trace metals
	boiler steamside wash	59 500	-	-	-	possible organometallic species
	coal pile runoff	28 400	13 800	10 800	2.63	low pH, dissolved trace metals
	filter backwash	136	99.6	180	0.756	good correlation apparent
	cation exchange regenerants	12 300	1 466	97 000	0.127	very low pH, imbalance in TDS components
	anion exchange regenerants	18 200	37 600	10 000	1.82	very high pH, imbalance in TDS components
	ash site runoff	1 410	1 400	1 600	0.881	possible trace metals
	bottom ash system blowdown	1 820	1 470	2 500	0.728	possible trace metals
	boiler room sump	1 600	1 670	2 900	0.552	good correlation apparent
	condensate polisher regenerants	28	75.5	600	0.047	low "f" factor compared to natural waters
	cooling water	25 000	25 300	60 000	0.417	good correlation apparent
	FGD disposal site runoff	3 440	-	3 300	1.042	high "f" factor compared to natural waters
	FGD system blowdown	15 000	-	11 000	1.364	high "f" factor compared to natural waters
Western	coal pile runoff	800	750	1 020	0.784	possible trace metals
	filter backwash	136	99.6	180	0.756	good correlation apparent
	cation exchange regenerants	9 200	7 060	35 000	0.263	low pH, imbalance in TDS components
	anion exchange regenerants	18 000	42 300	68 000	0.265	high pH, imbalance in TDS components
	ash lagoon overflow	1 500	1 540	1 870	0.802	possible trace metals
	boiler room sump	1 700	1 810	1 850	0.919	high "f" factor compared to natural waters
	condensate polisher regenerants	28	75.5	600	0.043	low "f" factor compared to natural waters
	R/O rejects	1 850	1 820	2 300	0.804	good correlation apparent
	cooling tower blowdown	11 100	-	-	-	good correlation apparent

Note: * calculated factor to convert conductivity to TDS

As described in the previous section, one analytical method used to determine the TDS involves the application of a factor to a conductivity measurement. In natural waters, this factor typically ranged between 0.5 and 0.75. In the case where good agreement occurred between the $TDS_{(e)}$ and $TDS_{(a)}$ values, the "f" factor was close to that observed for natural waters. For example, for the boiler room sump the $TDS_{(a)}$ of 1670 mg/L agreed closely with the $TDS_{(e)}$ of 1600 mg/L and the "f" factor relating conductivity to $TDS_{(e)}$ was 0.552 which was in the range found for natural waters.

In contrast, for the air preheater washwater the $TDS_{(e)}$ was significantly greater than the $TDS_{(a)}$ value and the "f" factor was 3.08, far greater than any value observed in natural waters. This wastewater was also significantly different in composition compared to natural surface waters. Similar results are apparent when the cation exchange regenerants are considered where the apparent "f" value is 0.127.

In summary, the TDS concentrations of wastewater from coal-fired power stations are usually much higher than those normally encountered in natural surface waters and are often significantly different in terms of their composition. However, there are some exceptions.

The "f" factor which relates conductivity measurements to $TDS_{(e)}$ concentrations gave good results when applied to water of composition similar to those found in natural surface waters. In contrast, greatly differing "f" values were apparent for wastewaters whose composition was very different from those found in nature. Consequently, conductivity measurement of TDS is most useful for monitoring wastewaters which are similar to natural surface waters with regard to TDS aid whose TDS constituents to do not vary significantly from those of natural TDS. They may also be useful for monitoring abnormal TDS content wastewaters whose contents do not vary significantly and for which an appropriate stream specific "f" value has been determined. In both cases, the nature of the TDS constituents and the variability in the stream must be determined in advance by more extensive specific component analyses.

$TDS_{(e)}$ concentrations in power station wastewaters were greater than those levels which have been shown to cause adverse effects on aquatic species. For this reason treatment may be required to reduce TDS components in various wastewaters before discharge in order to prevent deterioration of the receiving aquatic environment. A variety of treatment methods are available for this purpose.

5 TREATMENT OF WASTEWATERS CONTAINING DISSOLVED SOLIDS

5.1 Introduction

Total dissolved solids concentrations are an emerging concern for service and wastewater management at coal-fired steam electric generating stations. New and existing technologies in some cases have been shown to produce waters with very high dissolved solids concentration.

Each process for the removal of TDS requires, to a greater or lesser degree, some form of pretreatment and an acceptable method of waste brine or salt disposal. Economic or technical comparisons which do not consider these factors are meaningless if the difficulty of selection and operation of these accessary systems is greater than that of the TDS removal technology itself.

In addition, the level of acceptable TDS removal depends on whether the treated wastewater is to be discharged or reused in the generating station. Wastewaters to be recycled or reused need to be treated to remove problem chemical species from an operating perspective while those wastewaters to be discharged should be free of all significant levels of environmentally deleterious chemical species.

In zero discharge applications all of the waste solids, both dissolved and suspended must be impounded in suitable storage facilities. Studies have shown that unless there is a natural geological formation that favours low costs evaporation pond construction (assuming that evaporation occurs), a process which concentrates the dissolved solids and returns water to the station for consumptive use is the most economical option. The incentive is for processes to concentrate the dissolved solids to produce the smallest possible volume of wastewater or brine and reduce ultimate disposal costs.

Regardless of the treatment process, the salts and other waste products must be stored in ponds or otherwise disposed of. The lowest storage volume is required when precipitated crystals are stored as a thickened slurry with the interstices filled with saturated brine. Pretreatment generates significant amounts of waste and can easily double the volume of sludge produced for disposal. This favours processes which can recover large fractions of the water without pretreatment and, which also produces a slurry of salt crystals.

This section of the report presents a brief introduction to a number of the many alternatives for the removal of dissolved solids from wastewaters at coal-fired

steam electric generating stations. These are broadly classified as non-membrane and membrane processes and include the following:

Non-membrane Processes

- Change of Phase Separation
  - freeze crystallization,
  - atmospheric freezing for water desalination, and
  - distillation/evaporation
- Chemical Precipitation/Softening
- Ion Exchange Demineralization

Membrane Processes

- Reverse Osmosis
- Ultrafiltration
- Electrodialysis

Brine disposal methods, an important element in a complete dissolved solids treatment system, are also described. Detailed engineering design and cost comparisons are beyond the scope of this work.

5.2 Non-membrane Processes

Several non-membrane processes for the removal of dissolved solids involving a change of phase separation process have been developed for petrochemical refining and seawater desalting applications. The similarity between seawater and wastewater applications, centered around the basic chemistry and physical properties, makes these processes suitable for wastewater recycling applications. Other non-membrane processes not involving a change of phase such as chemical precipitation softening and ion exchange, are also described in this section.

5.2.1 Freeze Crystallization Technology. Change of phase separation processes such as freeze crystallization have a number of advantages over physical separation or membrane processes. Freeze crystallization has long been recognized and used where separation characteristics due to similar volatilities make vapour/liquid separation difficult. Another advantage of the process is its energy consumption which is low because the latent heat of fusion is about 19 percent of that for vapourization and the

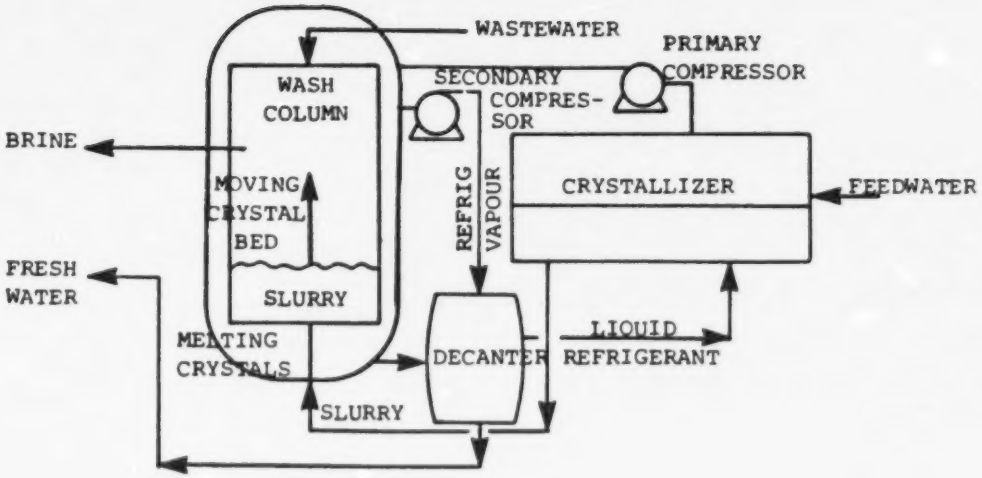
freezing process uses a heat pump cycle to transfer heat (Heist, 1981). Other advantages include:

- no requirement for wastewater pretreatment, therefore; co-precipitation is not a concern;
- minimization of the final waste volume, since pretreatment (addition of related chemicals) is not required;
- minimization of corrosion and scaling, because the process is conducted at low temperatures consequently expensive materials and construction are not required;
- a possible high level of water recovery;
- enhancement of by-product recovery from low temperature operation, since most compounds have an inverted temperature/solubility relationship in water;
- no need for large metallic heat transfer surfaces (or their maintenance) because most of the heat transfer occurs by direct contact (Heist, 1981; Barduhn, 1975).

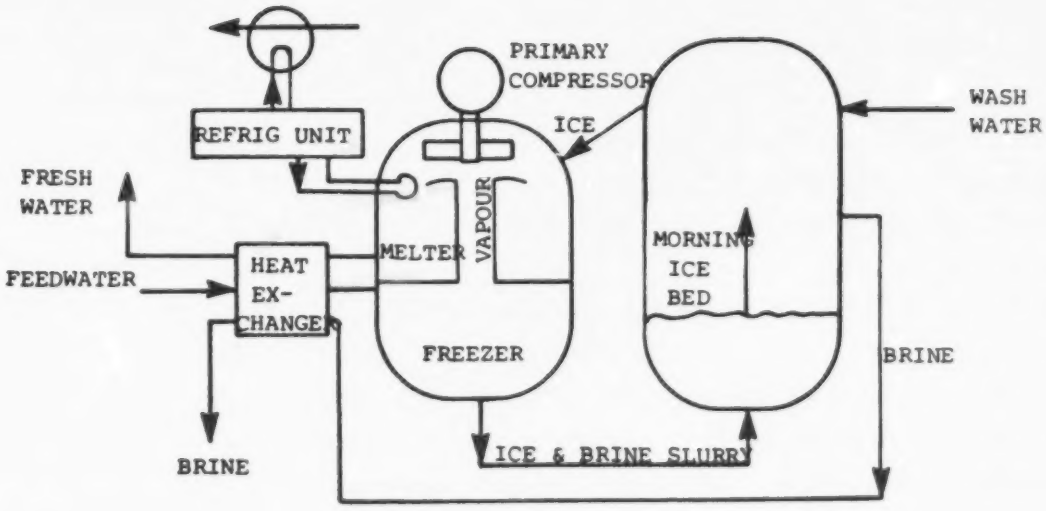
There are two general forms of the freezing process, one in which the water is the refrigerant (VFVC or vacuum flash compression) and one where the refrigerant is butane or a halogenated ethane (SRF or secondary refrigerant freezing) (Figure 12).

The functions that all freeze separation processes must perform in making a separation are:

- crystallization of one or more of the components of the solution;
- separation of the crystals from the remaining liquid and removal of any soluble impurity in the solids and/or the film of impure liquid coating the crystal;
- melting the crystal to recover the latent refrigeration from its phase change;
- refrigeration, in most cases, with a heat pump to remove heat from the crystallizer and transfer it to the matter;
- heat rejection, often as part of the refrigeration system, to remove ambient leaks of heat and mechanical energy input from processes equipment, from the system to cooling water; and
- heat recovery from the cold melted crystal and concentrated impurity streams minimizes refrigeration requirements (Heist, 1981).



SECONDARY REFRIGERANT FREEZING



VACUUM FLASH DIRECT FREEZING

FIGURE 12 VACUUM FLASH COMPRESSION AND SECONDARY REFRIGERANT FREEZING PROCESSES

The feed enters through the feed heat exchanger where it is precooled with cold melt and concentrated impurity stream. In the crystallizer about 15 percent of the liquid is converted to crystal. The crystal slurry is pumped to the wash column where the brine is separated and the crystals are purified and harvested. The impure solution stream continues to be recycled through the process until the degree of recycle desired is reached. The crystals are melted and a small amount recycled to the wash column for washing impurity from the crystal surfaces. Some form of refrigeration is used to transfer the heat from the crystallizing material into the melting crystals. Excess heat in the process is rejected to ambient cooling water.

Energy and capital are the two largest costs associated with freeze crystallization. A direct contact process is more energy efficient than any indirect process. The absence of any heat transfer surface should also be an economic plus, especially in large plants where economics of scale favour tanks rather than heat exchangers. Flow diagrams and mass and energy balances must be developed to determine the energy requirements and amount of by-products. For large flow applications, in excess of 40 m^3/h, the advantages of multi-stage operation begin to effect the economy of scale advantages (Heist, 1981).

When considering an application for this process, solid/liquid equilibria are required. These are used to determine the freezing point depression, the degree of water recovery desired and co-precipitation of any of the impurities. No heat is required for the process, but power is required for the two compressors. This amounts to about 38 MJ/m^3 of freshwater produced. The most important improvements in the process result from increased compressor efficiency (Fraser and Emmerman, 1970).

Colt Industries operated a truck mounted 57 m^3/day capacity freeze crystallization unit for TDS control in brackish water (Jhawar and Fraser, 1970). The raw water contained 3000 mg/L $CaSO_4$ in total dissolved solids of 15 800 mg/L (the high $CaSO_4$ content makes a wastewater particularly difficult to desalt). Without pretreatment, this unit gave an 80 percent yield of freshwater with a brine product of 8 percent salt. More detailed studies on this pilot-plant have been reported by Koretchko and Hajila (1972) and Koretchko (1972).

Heist (1981) described the application of freeze crystallization for the treatment of cooling tower blowdown. In this example, the wastewater was assumed to contain 7200 mg/L TDS which was slightly less than saturated with calcium sulphate and

silica. A two-stage freeze crystallization system was proposed and an ultimate water recovery of 95 percent assumed. In this application it was determined that the purified water would have a TDS of 200 mg/L while the brine from the system would have 110 000 mg/L TDS and 70 000 mg/L suspended solids due to the precipitation of calcium, sulphate and silica. Although more detailed costing information are presented elsewhere, Heist (1979) concluded that, crystallization was a lower cost alternative than pond disposal. This advantage occurred in spite of the low construction costs for the lined pond and very favourable assumptions about evaporation rates from the ponds.

5.2.2 Atmospheric Freezing for Water Desalination. As mentioned in the previous section, direct change of phase processes are more efficient than indirect processes. Energy and capital costs are the largest factors in the economics of the direct systems.

Atmospheric freezing for water desalination is an attempt to use the same principle as employed in the freeze concentration process. Freezing of a water solution results in the formation of a relatively pure ice and a more concentrated solution. However, in this case, low temperature air is used to freeze the saline water on an annual batch process basis. The ice is collected and the trapped brine is drained from the ice. The purified water is collected as the ice melts.

This concept has been in use in the Soviet Union for drinking water purification while in the United States, atmospheric cooling has been used to separate $NaSO_4$ from brines. Studies of the process have been conducted in the Soviet Union (Geller, 1962; Mitin, 1963), Canada (Szekely, 1964), and the United States (Stinson, 1964).

Using shallow reservoirs in Saskatchewan, Szekely (1964) was able to produce a ten-fold decrease in salt concentration, however, the process produced a limited amount of water per unit pond area. Elmore (1968) investigated atmospheric freezing at Laramie, Wyoming. Experiments were conducted at the 3800 m^3 scale on a water which contained high concentration of sodium sulphate. The TDS in the feedwater was reduced from 2380 to 410 mg/L producing a brine containing 51 200 mg/L.

Studies by the U.S. Bureau of Reclamation in 1973 evaluated a 9.5 m^3/min pilot plant atmospheric freezing system (Stinson, 1977). Agricultural sprinklers were used to spray the feed water upon a 10-acre site where ice accumulated. The brine was allowed to run off and was captured in a holding pond. Table 8 shows the chemical analyses of the feed, brine and produce water. A 98 percent reduction in TDS was achieved.

Stinson (1977) discussed the possibility of using this process to reduce the TDS in a small river system by diverting and treating the low flow, high TDS water. It was

TABLE 8 PERFORMANCE OF ATMOSPHERIC FREEZING SYSTEM (Stinson, 1977)

	Feed	Product	Brine
Calcium	311	15.4	620
Magnesium	164	1.7	403
Sodium	667	4.2	1518
Potassium	3.9	1.2	12
Carbonate	0	0	0
Bicarbonate	356	53.1	689
Sulphate	2464	9.6	5616
Chloride	66	0	152
TDS	4031.9	85.2	9010

results expressed in mg/L

suggested that a 25 percent reduction in TDS could easily be achieved. However, the climatic effects of such a process would have to be considered. The freezing of 950 m^3/min of water would release more heat than a 2000 MW power plant. The moderating effect on the climate would be 10 times that of a lake of equivalent area (Stinson, 1977).

5.2.3 Distillation/Evaporation Technologies. Distillation and evaporation technologies are commercially available for the desalination of seawater and for the concentration of process wastewaters for a number of industries. The primary purpose of evaporative treatment of wastewater is to produce a distilled stream that is sufficiently pure either for recycling in the plant or for discharge to the environment and a concentrated solid contaminants stream of the smallest possible volume. A well designed evaporator system coupled with a polishing demineralizer is capable of producing a very high purity feed water and a very concentrated waste stream. In the case of wastewater evaporation technology equipment, reliability and cost of maintenance are of greatest importance. Minimum contact between the equipment and the fluid being concentrated is also desirable (Rose, 1975).

Pretreatment of some form is usually necessary before wastewater can be fed to an evaporator. This may include filtration to remove suspended solids that might plug

pipes, values and heating surfaces as well as addition of anti-foaming agents and pH adjustment to minimize corrosion. Usually, filtration to 100 µm or less is required (Rose, 1975). The addition of anti-foaming agents can improve the ability of the evaporator to produce high quality distillate. Where wastewater acidity or alkalinity varies, a continuous pH monitor and control system is used.

During the distillation process sufficient heat is transferred to the wastewater to cause vapourization thus separating the water from the dissolved solids. For pure water, the amount of energy required to evaporate a unit mass of water at constant pressure and temperature is known as the heat of vapourization and is equivalent to 40.7 kJ/mole.

Equipment design features a closed tank traversed by steam coils, with a moisture separator at the outlet (Rice and Strauss, 1977). Vapour condensed in a separate heat exchanger provides reusable water of high purity. In flash evaporation, a variation on this technique, only a partial vacuum is applied to the tank. Incoming water is preheated to just the proper temperature so flashing ensues immediately upon its entry into the chamber.

When two or more such units are used in series, the combination is a multi-effect evaporator. Steam produced by one stage is condensed in the heating coils of the next stage which is operated at a lower pressure. Purified water from both stages flows to a common outlet. The less costly single-effect units produce more water for a given amount of evaporator-tube surface, and are preferred if the product is to be used for boiler makeup.

Vapour-compression evaporators, a third type, are coming into wide use. The design comprises a boiling chamber, a heater to initiate the reaction, a heat exchanger and a vapour compressor. Hot water passes from the exchanger to the chamber, where boiling takes place. The steam generated is moved to the compressor, where its pressure is raised slightly. Upon return to the evaporator, the steam condenses, giving up heat, which is used to evaporate additional water. Outgoing condensate passes through the heat exchanger to heat incoming feed.

Another design embodying vapour-compression is aimed primarily at increased concentration of the brine. Water fed to the evaporator sump is continuously recirculated to the top header, where it is distributed to the inside walls of vertical tubes as a thin film. The film runs down the walls and is evaporated. The resulting steam moves out through a demister to the compressor. The condensed steam cools and condenses on the shell side of the tubes, and release of its heat evaporates more water from the brine film

inside the tubes. After passing back through the heat exchanger the condensate usually contains less than 10 mg/L dissolved solids. A more recent version of this system features flat plates rather than tubes, removing 95 percent of the water from the brine.

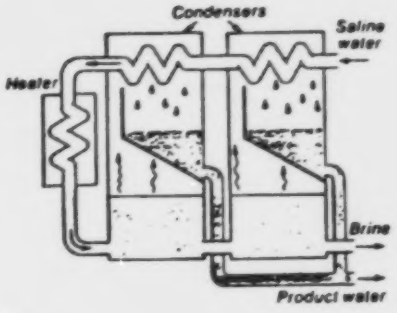
Figure 13 shows the configuration of the flash distillation (upper drawing), vapour-compression (middle drawing) and long tube evaporator (lower drawings) systems.

Conventional distillation equipment can produce several kilograms of product water for each kilogram of steam consumed. This performance ratio can range from 4:1 to 8:1, depending on the equipment design and operation (Awerbuck, 1977). The cost of operation of multi-flash evaporators for seawater desalination in terms of energy inputs is about 0.305 MJ/L of product water. The energy consumption for evaporation depends greatly on the amount of inert gases (air) in the water (Orivuori, 1980).

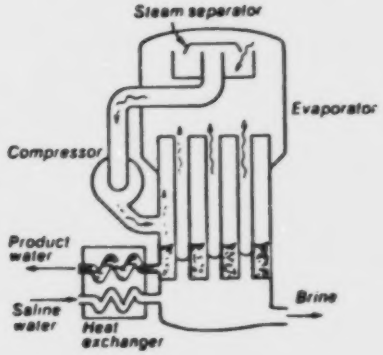
Morin and Latour (1979) noted that about half the total annual operating cost of a multi-stage flash evaporator system is a function of fuel cost compared to about 12 percent for a reverse osmosis system for the desalination of seawater. The operating cost considerations are thus related to current and projected fuel costs. The capital costs of these two systems at a 9500 m^3/d plant size were comparable (Awerbuck, 1977).

Several manufacturers currently produce evaporator equipment of each design configuration, however, vapour compression evaporators are most widely used in the power generation industry. The system for the treatment of cooling tower blowdown is shown in detail in Figure 14. The pH of the wastewater is adjusted to between 5.5 and 6.5 by the addition of sulphuric acid. The wastewater is pumped through a heat exchanger to recover the sensible heat from the distillate before being fed into a de-aerator to strip the water of non-condensible gases such as carbon dioxide, oxygen, and nitrogen. The steam and the non-condensible gases are usually vented to the atmosphere. After the de-aertor, the feed enters the evaporator sump where it is mixed with a concentrated slurry and recirculated to the top of the evaporator. It falls from there along the inside walls in a thin film. As the water falls, it partially converts to steam which is then compressed by about 14 kPa and used on the shell side as a heating medium. No additional source of heating steam is necessary except during start-up. The major energy requirement is the electrical power used in the compression of steam.

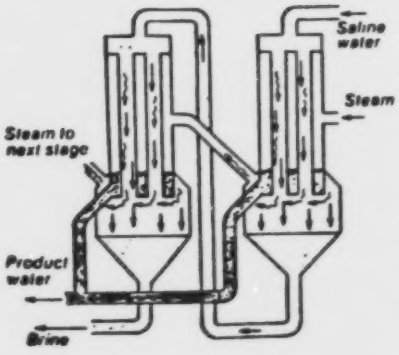
Steam exiting from the shell side is condensed and utlized as distillate. Normally 96 to 98 percent of the feed is recovered in the form of distillate with about 1 to 5 mg/L of dissolved solids present. The process has several advantages in application to coal-fired generating stations. Deposition of scale on plant equipment is prevented by introducing calcium sulphate crystals in the brine as nuclei on which the scale will deposit



Flash distillation vapourizes water to remove dissolved and suspended solids.



Vapour compression units boils heated water in a chamber then feeds steam to a compressor. The steam condenses upon re-entering evaporator, releasing heat to boil additional water. Condensate leaving chamber heats incoming wastewater.



Long tube evaporators condense purified water on the outer surfaces of vertical tubes.

FIGURE 13 CONFIGURATIONS OF DISTILLATION SYSTEMS (Rice and Strauss, 1977)

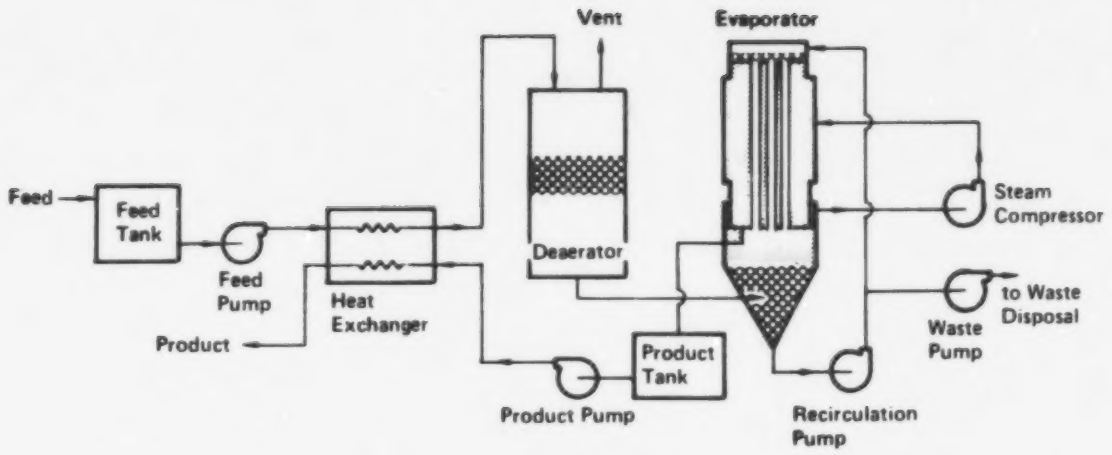


FIGURE 14 VAPOUR COMPRESSION EVAPORATION SYSTEM

in preference to equipment and piping. The process does not affect or change the chemistry of the cooling tower water. Since the cycles of concentration are not affected, the adverse effects of high total dissolved solids, sulphates, and chlorides are avoided. The vapour compression evaporator process is also more capable of handling wastewaters with changing characteristics than other processes.

At present the vapour compression evaporator is frequently used in the western part of the U.S. to achieve zero discharge wastewater systems. For example, at Hayden Generating Station, the cooling water blowdown concentration factor is approximately 40. The product which has less than 10 mg/L of total dissolved solids, is recycled to the polishing demineralizer for boiler makeup water and the excess is used as the cooling tower makeup. Table 9 lists seven power plants in the U.S. that are using vapour compression evaporators to treat cooling water blowdown (Anon., 1981).

Some plants also use vapour compression evaporators to treat other wastes such as concentrates from reverse osmosis units and ash pond blowdown. For example, at Ray D. Nixon Generating Station, the concentrate from a reverse osmosis unit is treated by the vapour compression evaporator for reuse within the station (Anon., 1981).

TABLE 9 POWER PLANTS USING VAPOUR COMPRESSION EVAPORATORS (Anon., 1981)

Station	Feed Rate L/s	Water Treated	Effluent Quality (mg/L TDS)
Navajo Generating Station Page, Arizona (1500 MW)	13	cooling tower blowdown	2
Craig Generating Station Craig, Colorado	38	cooling tower blowdown	
Hayden Generating Station Colorado (440 MW)	13.6	cooling tower blowdown	<10
Ray D. Nixon Generating Station Colorado Springs, Colorado (200 MW)	25	cooling tower blowdown and reverse osmosis concentrate	<5
Deerhaven Generating Station Gainesville, Florida (316 MW)		cooling tower blowdown and ash pond blowdown	
Colstrip Generating Station Colstrip, Montana (2268 MW)	21	cooling tower blowdown	
San Juan Generating Station New Mexico (1260 MW)	10 (later upgraded to 13)	pretreated blowdown from scrubber, ash system, and cooling water; pretreatment consists of chemical clarification; filtration and reverse osmosis	

The selection of evaporation technology depends on the characteristics of feed water, required operating simplicity and operating costs which include the energy costs of each system. Where electricity is less costly than steam, vapour compression is favoured because the major energy requirement in the process is to drive the vapour compressor. Where excess steam is available, multi-stage evaporators may be economically attractive since thermal energy is the greatest energy requirement for the process.

Vapour compression evaporators are currently being used at several generating stations in the U.S. primarily to treat cooling tower blowdown which is the largest wastewater produced in these plants. Several other stations use this process to concentrate other plant wastewaters as well.

5.2.4 Chemical Precipitation/Softening Technology. Softening is a process involving chemical reaction and precipitation to alter the chemical composition of a wastewater. Softening using lime and soda ash can reduce calcium, magnesium and silica which are major scale formers on heat exchange surfaces. The treatment of wastewaters by this process involves the stoichiometric exchange of the low solubility, hence scale forming compounds for those which have greater solubility such as sodium, chloride and sulphate. The net effect is that the treated wastewater can continue to be recycled many more times without scaling. This reduces the water intake requirement and the total water volume discharge from a system. The process is often used as a pretreatment step for membrane processes or evaporators to prevent scaling within the primary TDS removal system. Four configurations are possible (Anon., 1976):

1) **Cold Process:**
   a. sedimentation type (downflow); and
   b. sludge-contact type (upflow).

2) **Hot Process:**
   a. sedimentation type (downflow); and
   b. sludge-contact type (upflow).

Continuous sedimentation units are most often utilized to settle the precipitated chemical species. The raw water is thoroughly and continuously mixed with proportioned chemicals in a flash mixer which consists of a propeller-type agitator that operates in a relatively small chamber. Effluent from the mixer flows through a flocculation zone to ensure that the action of the slowly rotating paddles will form particles of proper size. The water then flows to a zone designed to settle the sludge effectively.

Figure 15 shows a sludge contact type clarifier which is commonly used in the cold softening process. The configuration of equipment used for hot softening process softening is shown in Figure 16.

The performance of the cold lime soda softening process is closely tied to the operation of the clarifier. Such systems are not amenable to automatic controls and require significant operator attention. As with any clarifier process, fluctuations in the

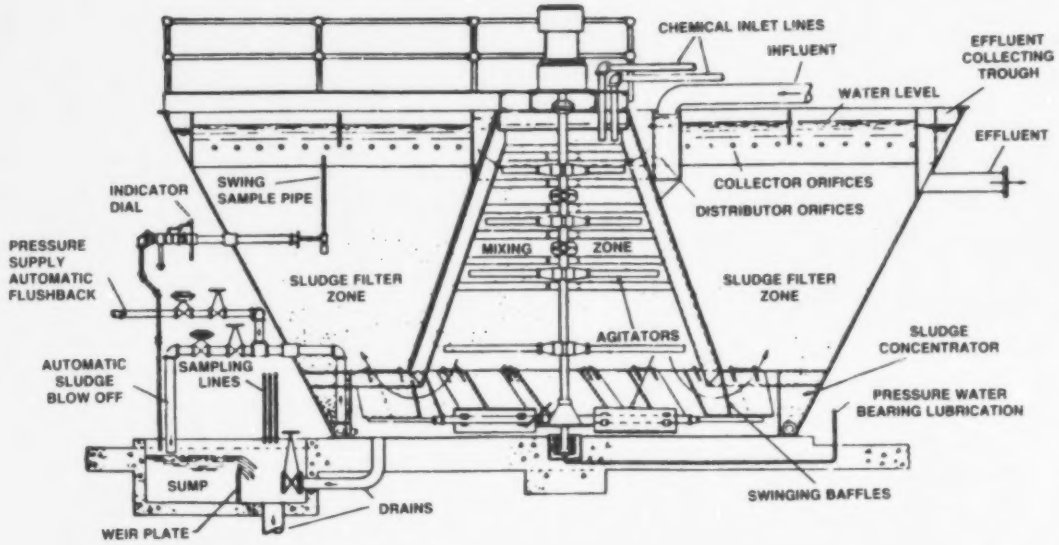


FIGURE 15 SLUDGE CONTACT CLARIFIER USED IN COLD LIME SODA SOFTENING (Anon., 1976)

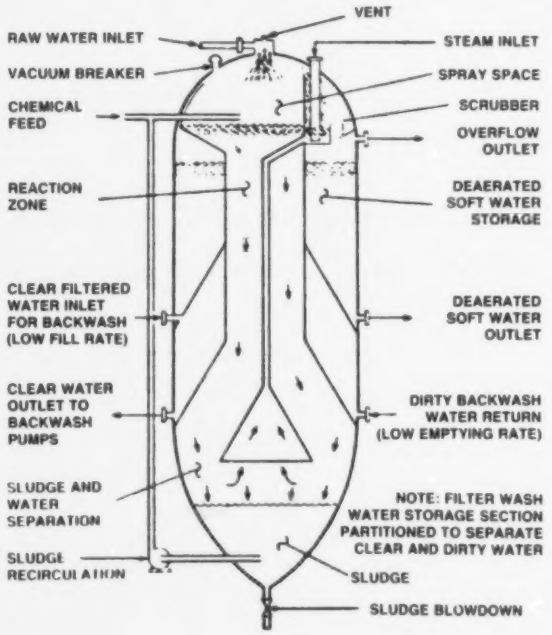


FIGURE 16 HOT LIME SODA SOFTENING PROCESS EQUIPMENT (Anon., 1976)

feed quality or flowrate can have great impact on the system performance. Frequent fluctuations can be expected when this process is applied to the treatment of wastewater. Design considerations should be made to reduce the frequency and intensities of such fluctuations.

The softening process has the ability to remove four impurities from wastewater. During the process calcium hardness precipitates as calcium carbonate and magnesium hardness as magnesium hydroxide. Bicarbonate alkalinity is converted to carbonate and is then removed as calcium carbonate. Silica is removed as insoluble silica magnesium complex when it reacts with magnesium hydroxide. Turbidity from suspended solids and magnesium hydroxide and calcium carbonate sludge are also removed by sedimentation. This process is adaptable to most wastewaters except those that are high in chlorides, sulphates or dissolved solids concentration (Matson, 1979). The process uses relatively low cost lime and soda ash materials.

The major drawback of this process is that very high salinities can result in the softened, recycled stream which may necessitate a desalting or brine disposal system for the ultimate blowdown from the system. The main advantage is that the wastewater salinity becomes an independent variable which is determined by process operation rather than wastewater chemistry. Although the higher wastewater salinities will lead to higher capital and operating costs, the opposite is true for water recovery/brine concentration systems. The higher the initial feed concentration, the lower the volume of water that must be finally treated or disposed of. Processes which permit the system to operate at increase salt concentrations, make economic sense (Westbrook and Writh, 1977).

During the lime-soda softening process, lime is added to raise the pH to between 10.5 and 11.0 units. At this pH, bicarbonate ion is converted to carbonate ion, which reacts with calcium ion to form calcium carbonate precipitate. Soda ash (Na_2CO_3) is added to the softening to make up for any carbonate deficiencies. Magnesium is precipitated as magnesium hydroxide. Dissolved silica is removed by adsorption onto the magnesium hydroxide floc. The treated water is then clarified, filtered, and pH-adjusted. Ions such as sodium, potassium, sulphate and chloride are not removed by the softening process.

The chemical reactions of the softening process are:

Carbonate Hardness

$Ca(HCO)_2$	+	$Ca(OH)_2$	=	$2CaCO_3$	+	$2H_2O$		
calcium bicarbonate		calcium hydroxide		calcium carbonate		water		
$Mg(HCO_3)_2$	+	$Ca(OH)_2$	=	$MgCO_3$	+	$CaCO_3$	+	$2H_2O$
magnesium bicarbonate		calcium hydroxide		magnesium carbonate		calcium carbonate		water
$MgCO_3$	+	$Ca(OH)_2$	=	$Mg(OH)_2$	+	$CaCO_2$		
magnesium carbonate		calcium hydroxide		magnesium hydroxide		calcium carbonate		

Non-carbonate Hardness

$MgSO_4$	+	$Ca(OH)_2$	=	$Mg(OH)_2$	+	$CaSO_4$
magnesium sulphate		calcium hydroxide		magnesium hydroxide		calcium sulphate
$MgCl_2$	+	$Ca(OH)_2$	=	$Mg(OH)_2$	+	$CaCl_2$
magnesium chloride		calcium hydroxide		magnesium hydroxide		calcium chloride

Reactants with Soda Ash

$CaSO_4$	+	Na_2CO_3	=	$CaCO_3$	+	Na_2SO_4	
calcium sulphate		sodium carbonate		calcium carbonate		sodium sulphate	
$CaCl_2$	+	Na_2CO_3	=	$CaCO_3$	+	2NaCl	
calcium chloride		sodium carbonate		calcium carbonate		sodium chloride	(Anon., 1976)

The efficiency of the softening reactions is greatly influenced by temperatures. Higher temperatures accelerate the reaction rates, increase the extent of completion of the reactions, and permit the reactions to be carried out at lower pH values (Anon., 1976). Hot process softeners require the raw water to be heated to or above 100°C usually by spraying the water into a steam atmosphere. The chemical reactions form precipitation almost instantaneously, and the high temperatures accelerate

sedimentation. The hot process has the ability to treat large volumes in a relatively small piece of equipment.

Ionic strength also effects softening chemistry. Higher ionic strengths reduce ion activities and the ion pairs formed during the chemical reactions do not participate in the softening reaction.

Figure 17 shows the relative performance of cold-lime soda and hot-lime soda softening when used to treat a raw water with a TDS of about 400 mg/L (Anon., 1977).

The softening process produces sludges primarily composed of calcium carbonate and magnesium hydroxide. The process has the ability to remove iron, manganese, and in the application to cooling towers, trivalent chromium and zinc, since these and other metals precipitate with the sludge.

Softening processes will not remove all TDS components from a wastewater; however, the wastewater can be softened to remove scale forming elements and thus permit higher cycles of concentration. This process could reduce hardness to between 5 and 80 mg/L as $CaCO_3$, but, depending on the use, additional treatment such as ion exchange may be required. A number of metals such as iron, zinc, and trivalent chromium will be precipitated during the chemical reactions. In general, lime softening is more difficult to control than other methods of softening such as ion exchange.

5.2.5 Ion Exchange Demineralization Technology. An ion exchange resin has the ability to exchange one ion for another, hold it temporarily in chemical combination, and give it up to a strong regenerating solution. Exchange takes place at equilibrium or with reversible reactions without structural change in the resin. During this exchange, electroneutrality is maintained in the solution-resin system.

Although considerable technological advances were made in ion exchange technology and applications to produce high quality water for power plants, there were limited applications for desalination of brackish water until the late 1960's.

During regeneration of a resin for demineralizer application, the affinity for the exchanged ion from solution at relatively low concentration is over-ridden by contact with a highly-concentrated solution of the original exchangeable species.

Present day demineralizer resins are almost exclusively based on either a styrene-divinyl benzene or acrylate-divinyl benzene copolymer where divinyl benzene acts as the cross-linking material. Ionic groups are attached to the polystyrene or polyacrylate matrix by chemical treatment. The resin will then act as a strong or weak base (anionic) or strong or weak acid (cationic) depending on the nature of the attached ionic group.

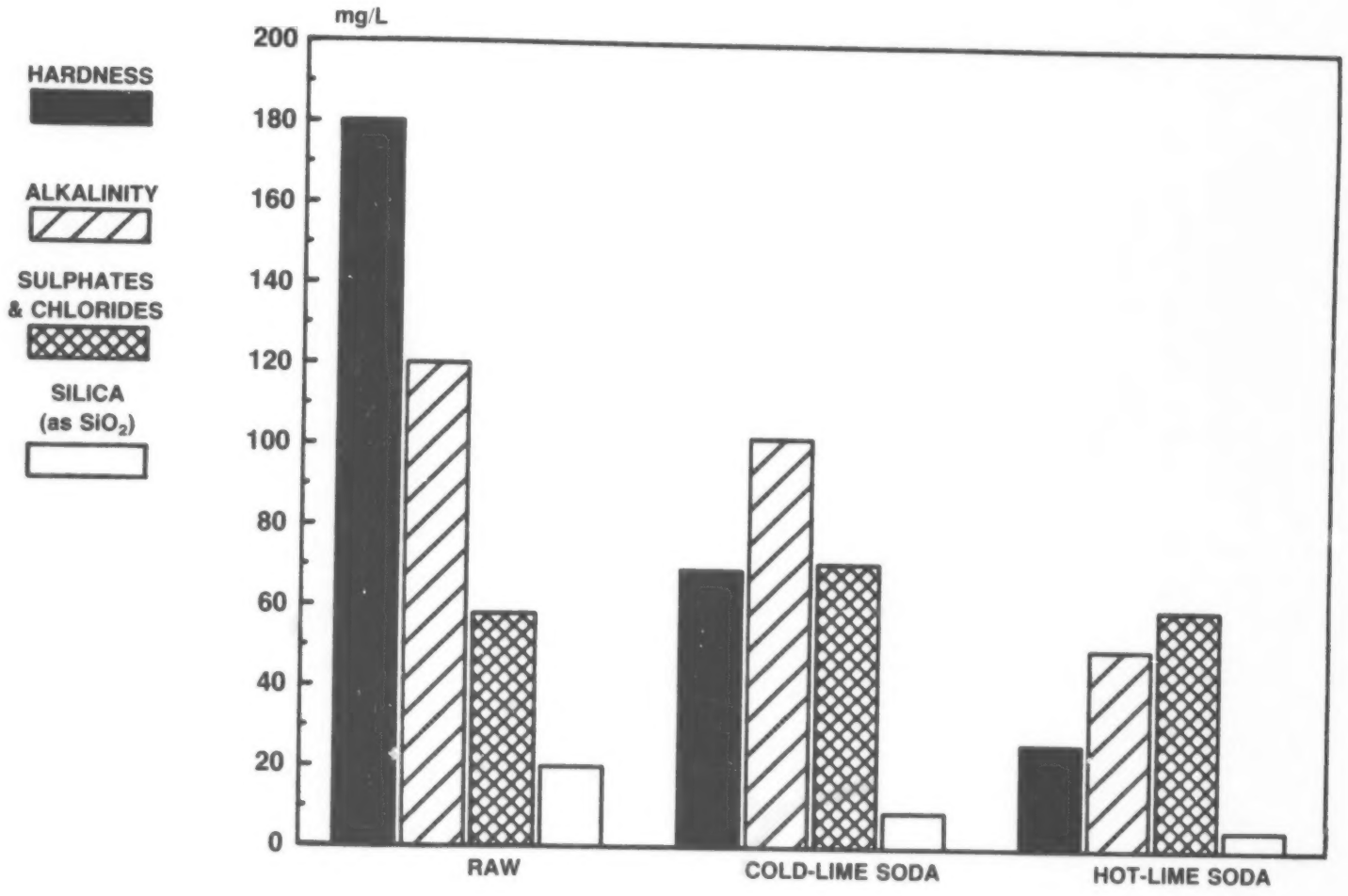


FIGURE 17 PERFORMANCE OF HOT AND COLD LIME SODA SOFTENING (Anon., 1977)

Two bed ion exchange demineralization consists of a cation exchange resin in the hydrogen or acid form in the first bed and an anion exchange resin in the hydroxyl or base form in the second bed. The water passes through the first bed cation exchanger while the cations are exchanged for the hydrogen following the equation (Lynch and Mintz, 1972).

$$R - H + Na^+ + Cl^- \rightarrow R - Na + H^+ + Cl^-$$

The strongly acidic effluent from the first bed is passed through the second bed (anion exchanger) where the anions of the acid exchanger are exchanged for hydroxyl groups, which in turn combine with the hydrogen ions to form water and a neutral product.

$$R - OH + H^+ + Cl^- \rightarrow R - Cl + H^+ + OH^- \; OH^- + H_2O$$

In this system the cation exchanger is normally regenerated with an acid (such as sulphuric) and the anion exchanger is regenerated with an alkali (such as sodium hydroxide) to restore the beds for further demineralization. Use of high quality rinse water to remove excess regenerants is a normal part of the regeneration step.

In practice, a strong acid and base exchanger will be used in series to remove the bulk of the total dissolved cationic and anionic solids, respectively. Weak acid and base exchangers can be placed at different points relative to the above units depending on whether a rough pretreatment or polishing treatment is required. In either case, the incentive to employ the less efficient weak acid or base exchanger lies with a significantly increased regeneration efficiency and reduced operating costs. A mixed cationic/anionic resin exchanger can also be used for effluent polishing. In addition, a specific exchanger can be operated in one of three contacting modes:

a) **Fixed Bed**

The downflow fixed resin bed technique is predominant for process water demineralization after pretreatment for suspended solids removal. It achieves intimate solution/resin contact while acting as a filter. Ion breakthrough or exhaustion and regeneration follow each other intermittently. It has the disadvantages of susceptibility to suspended solids fouling and the requirement of a duplicate system to operate during regeneration.

b) **Fluidized Bed**

The fluidized bed, while reducing solution/resin contact, allows passage of suspended materials. In addition, regeneration can take place in the downflow fixed bed mode

for increased efficiency. A duplicate system is required for continuous demineralization while the other is being regenerated.

c) **Continuous or Moving Bed**

In this mode, water is "upflow-fed" in pulses or continuously such that fluidized resin leaves the exchanger, is regenerated in a similar unit and returned to the exchanger continuously. The main advantages are higher efficiency of regeneration, elimination of potential regenerant leakage into effluent, reduced capital cost since no duplicate system is needed and reduced resin inventory requirement for high-solids or brackish waters through higher recycling rates. Disadvantages are greater complexity and controls, attrition losses depending on frequency of pulses, recycle rate and susceptibility to suspended solids fouling for low-frequency pulsed systems.

Empirical rules have been developed to describe the behaviour of ion exchange resins.

1) At low aqueous concentrations and ordinary temperatures, the extent of exchange or the exchange potential increases with increasing valence of the exchanging ion.
($Na^{+} < Ca^{++} < La^{+++} < Th^{++++}$)

2) At low aqueous concentrations, ordinary temperatures, and constant valence, the exchange potential increases with increasing atomic number.
(Li < Na < K < Rb < Cs; Mg < Ca < Sr < Ba; F < Cl < Br < I)

3) At high concentrations, the differences in exchange potentials of ions or different valence diminish and, in some cases, the ion of lower valence has the higher exchange potential.
(Na^{+} vs Ca^{++})

4) At higher temperatures or at high concentrations, the exchange potentials of the ions of similar valence do not increase with increasing atomic number but are very similar, and level off or even decrease.

5) The exchange potentials of various ions may be approximated from their activity coefficient (that is the deviation of the solution from ideal thermodynamic behaviour). The higher the activity coefficient the greater the potential.

6) The exchange potential of the hydrogen ion or the hydroxyl ion depends upon the strength of the acid or base formed between the functional group and the hydrogen or hydroxyl ion; the stronger the acid or base formed, the lower the potential.

7) Organic ions of higher molecular weight and metallic anionic complexes exhibit unusually high exchange potentials.

8) As the degree of cross-linking or the fixed ion concentration of any ion exchange is lowered, the exchange equilibrium or selectivity coefficient approaches unity.

The overall efficiency of the ion exchange process can be significantly affected by the degree of wastewater pretreatment. Unless the wastewater is relatively free of suspended and colloidal material, poor utilization of the exchange bed will result. These materials form a mat at the surface of the bed and increase the pressure drop through the column. This usually leads to channeling and bypassing of portions of the bed. The individual beads may also become coated and reduce the rate of diffusion of ions in and out of the exchange particle resulting in poor kinetics. In a similar way, traces of oil and gases in solution can also result in channeling and loss of resin during backwashing (Anon., 1974).

Changes in temperature affect both the hydraulics and kinetics of ion exchange process operation. The overall rate of exchange doubles with each 30°C rise in temperature. This is particularly significant for weakly basic and acidic exchangers. As the temperature of the wastewater changes, the bed expansion and pressure drop characteristics also change. The hydraulics can be affected due to change of viscosity of water with temperature. Increased temperature of water decreases viscosity, decreases pressure drop and significantly reduces bed expansion (Anon., 1974).

Ion exhange is a chemical reaction between the ion in solution and the resin. One equivalent weight of dissolved solids is removed from solution by an equivalent weight of resin which is usually termed the exchange capacity and is expressed in meq/mL (milliequivalents per millilitre) or grams $CaCO_3$ removed per cubic metre of resin. The number of hours that a bed is in service before regeneration is an economic variable and is determined by balancing the capital cost of the bed and vessel against the cost of regeneration, labour and losses due to efficiencies (Prengle et al., 1975).

In practice, most commercial resins require bed volumes to be large enough to limit flow rate to 4 to 10 $L/s \cdot m^3$. Convention dictates that loading rates should be limited to 0.33 to 0.67 to limit pressure loss, however, higher loading rates are feasible (Koenig and Jureski, 1968; Prengle et al., 1975). The resin bed should be at least 0.7 m in depth. Deeper beds require greater pumping power but in shallower beds it is more difficult to evenly distribute the flow. A diameter to depth ratio of 3 is suggested.

The vessel volume must exceed the volume of the resin to allow for bed expansion during backwashing, regeneration and rinsing. Backwashing removes suspended solids in the feedwater and prevents accumulation in the bed.

Anionic resins can be regenerated with a dilute solution of sodium or ammonium hydroxide while cationic resins require dilute sulphuric acid. The regenerants are usually 4 to 5 percent solutions. Both resins require 110 percent of the theoretical volumes and are usually reused at a flow of about 134 L/m^3 of water (Prengle et al., 1975).

The capital cost of an ion exchange system depends on the volume of the water treated and the $CaCO_3$ equivalent of total dissolved solids of the feedwater. The capital cost remains constant for a particular flow rate until a critical TDS value is reached. The reason is that for a given flow rate, a minimum volume of resin vessel volume is required for a given maximum loading rate.

Economic studies have been conducted comparing evaporators and ion exchange demineralizers to produce water of sufficiently high quality for use as boiler feedwater. These studies include the following factors: the cost of fuel, costs of chemicals for the pretreatment before evaporator or demineralizer and for demineralizer regenerants, the cost of replacing the demineralizer resins, the cost of maintenance and operating labour, the equiment costs, including erection and the building for its housing, and the cost of the power lost through degradation of the extracted steam used for the evaporator (Applebaum, 1968).

Ion exchanger demineralizers are more economical when fuel cost is higher and when the TDS concentrations are lower (less than 500 mg/L), especially when the alkalinity of the water is large in proportion to the total dissolved solids present. Evaporators, for this application, are more economical when the TDS in the water is greater than 500 to 1000 mg/L.

Ion exchange demineralization when used for the desalination of wastewaters has the advantage over other systems that it is basically simple and easy to operate; capital investments are comparatively low, the process operates smoothly with few of the mechanical problems associated with other systems and corrosion is minimal.

Ion exchange by nature is capable of complete demineralization, and it is this special capability that results in its frequent use as a post-treatment polishing stage even for distillation processes. Blending with raw feed is therefore a possibility.

Although ion-exchange resins are vulnerable to organic fouling similar to membrane processes, they are less affected by iron and manganese contaminations and do not require the pH adjustment of the feedwater as do the membrane processes.

The chief disadvantages of ion-exchange demineralization are that costly regenerants are required and the amount of regenerants is proportional to the salts removed, which limits the total salinity that can economically be removed from a brackish water. Because of this, ion exchange is restricted to the demineralization of water of comparatively low salinity.

Related to the regenerant requirements is the ratio of the volume of product obtained to the volume of resin waste that results from effective regeneration and rinsing of the beds. This ratio varies considerably with total mineral reduction. Typically, for a mineral reduction of 1500 mg/L (as $CaCO_3$), 80 percent recovery of product is possible, but for a mineral reduction of 4000 mg/L (as $CaCO_3$), only 50 percent recovery may be expected (Lynch and Mintz, 1972). Ion exchange also produces a greater waste disposal problem than membrane processes because there is a need to dispose of the regenerant chemicals in additional to the salts present in the feedwater.

The regeneration of the conventional ion exchange bed requires at least an equivalent amount of chemical for each equivalent of exchanged salt. In the case of strongly ionized exchangers, the regeneration usually requires at least a two-fold excess. For a typical deionization process, under the best conditions, two equivalents of electrolyte will be generated for each equivalent of salt removed (Prengle et al., 1975).

Where weak acid or base resins can be used, a significant reduction in waste can be realized since theoretical regeneration levels are approximately one equivalent of waste per equivalent of salt removed. The waste will be several orders of magnitude more concentrated than that of the stream treated (Fisher and McGarvey, 1976). Thus, it can be reasonably expected that the salt load in the wastewater will double. The significance of this will depend on the brine disposal facilities for the given site.

Until the mid-nineteen sixties little practical progress had been made toward establishing ion exchange as a desalting process. The general assumption was made that ion exchange was restricted by economics to waters of less than 1000 mg/L TDS; however, various systems under development began to evolve to the practical stages for desalination by the late sixties. Significant among these systems was the development of superior resins such as the weak-base anion-exchange resins which provided greater flexibility in the choice of regenerant and produced greater regenerant efficiency. Initially, the regeneration step consumed as much as 300 percent of the stoichiometric amounts of

regenerant chemicals. In recent years, regenerant requirements as low as 100 percent of stoichiometric amounts have been reported (Lynch and Mintz, 1972).

5.3 Membrane Processes

A membrane separation process is based on the selective transport of a chemical species through a semi-permeable membrane. The ability of some membranes to selectively pass certain species can be understood by assuming that species passing through the membrane must first dissolve in the membrane and then diffuse through it. The structure of the membrane determines the relative ease with which various species dissolve in and pass through the membrane (Tang et al., 1980).

The selectivity of some membranes seems to be based on solute size. It can be assumed that the transport mechanism is primarily that of a molecular sieve which is controlled by the size and shape of the pores compared to the size and shape of the solute molecules. The driving force for transport through the membrane can be pressure, concentration or electrical gradients.

Three membrane processes: reverse osmosis, ultrafiltration and electrodialysis, can be used to treat wastewater containing dissolved solids. Each of these processes separates the feedwater into a concentrated and a purified stream. In terms of energy, each process must overcome the free energy of mixing. The function and driving forces for each of the processes are summarized in Table 10 and schematic drawings of the three membrane separation processes are shown in Figure 18.

TABLE 10 MEMBRANE SEPARATION PROCESSES (Weber, 1972)

Process	Membrane Function	Driving Force
Reverse Osmosis	selective transport of water	pressure
Ultrafiltration	discriminates on the basis of molecular size, shape and flexibility	pressure
Electrodialysis	selective ion transport	electrical potential gradient

There is no clear distinction between ultrafiltration and reverse osmosis. Both processes remove solute from solution in a manner similar to the removal of suspended solids by filtration. Unlike a filter, however, the separated phase does not accumulate on the surface of the medium to any great extent but rather emerges in the form of a more

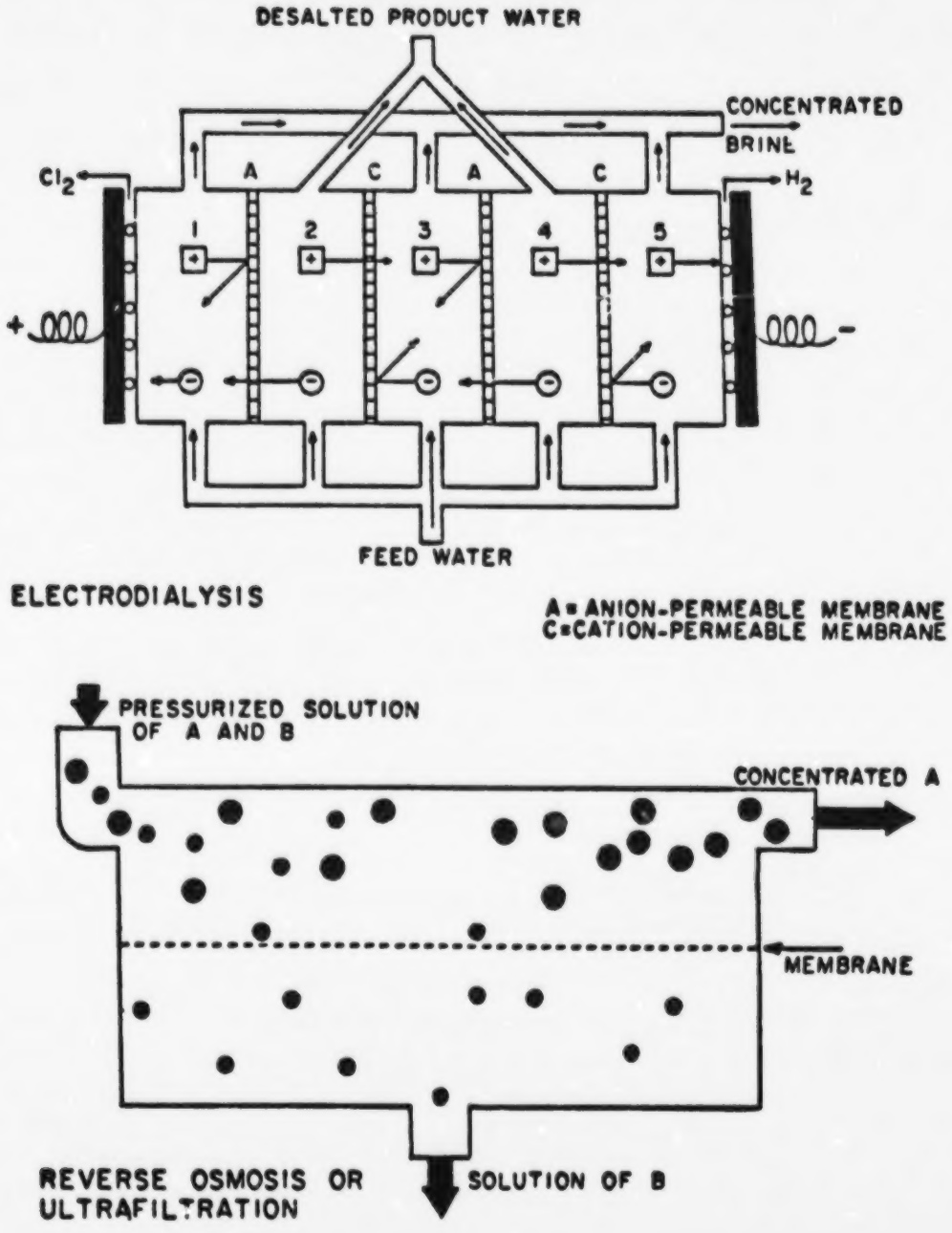


FIGURE 18 SCHEMATIC DIAGRAM OF MEMBRANE SEPARATION PROCESSES (Lacey, 1972)

concentrated solution while the permeate emerges as a diluted stream (Mulligan and Fox, 1976).

The three membrane processes are similar in that:

- permeation of materials through semi-permeable membranes achieves separation;
- there is similar feed, reject and product stream arrangement for continuous operation;
- there is no phase change;
- no heat is required for the separation process;
- boundary layers effects or concentration polarization tend to occur; and
- membrane fouling is possible.

Differences in the membrane systems include:

- the driving force for reverse osmosis and ultrafiltration is pressure, for electrodialysis it is electrical potential;
- reverse osmosis and ultrafiltration separate colloidal materials with high molecular weight solutes, whereas, electrodialysis can transfer only ions;
- the power required for reverse osmosis and ultrafiltration is approximately proportional to the product water flow but is not sensitive to variations to the dissolved solids concentrations of the feed; the power required for electrodialysis is nearly proportional to the amount of salt removed but is only slightly sensitive to flow rate;
- reverse osmosis and ultrafiltration can remove 90 to 99 percent of solutes in one stage; electrodialysis can remove 25 to 60 percent per stage; and
- electrodialysis can concentrate brine to between 10 to 25 percent solids in one stage with a feed as low as 1000 mg/L; in contrast, reverse osmosis and ultrafiltration can concentrate feedwaters by a factor of less than 10 per stage and reverse osmosis is limited to a maximum concentration of about 70 000 mg/L.

5.3.1 Reverse Osmosis Technology. When a semi-permeable membrane is placed between two solutions of different salt concentrations, water normally flows from the dilute side through the membrane to the more concentrated side in order to maintain equilibrium. The driving force behind this process is known as the osmotic pressure.

In the reverse osmosis treatment process, the pressure on the liquid with the higher concentration is increased sufficiently to force the water to flow to the dilute side. The net result is that the concentrated side becomes more concentrated with dissolved solids while the dilute side becomes more dilute. This separation process also known as hyperfiltration has been used in the removal of total dissolved solids from water since the early 1970's. There are three basic design configurations for commercial Reverse Osmosis membranes:

1) **Spiral Wound RO Membranes**

The spiral wound membrane has a relatively high ratio of membrane area to pressure vessel volume (Figure 19). The membrane is supported on both sides of a backing material and sealed with glue on three of the four edges of the laminate. The laminate is also sealed to a central tube, which is drilled. The membrane surfaces are separated by a screen material which acts as a brine spacer. The entire package is then rolled into a spiral configuration and wrapped in a cylindrical form with tape. Feed flow is parallel to the central tube, while the permeate flow is through the membrane toward the central tube.

2) **Hollow Fibre RO Membranes**

The hollow fibre type of membrane has fine aromatic, polyamide fibres about the size of a human hair with an inside diameter of about 0.05 mm and an outside diameter of 0.10 mm (Figure 20). In these very small diameters, fibres can withstand enormous pressures.

In an operating process the fibres are placed in a pressure vessel with one end sealed and the other protruding outside of the vessel. The saltwater is under pressure on the outside of the fibres and product water flows inside the fibre to the open end (Figure 21). For operating plants, the membrane modules are assembled in a configuration similar to the spiral wound unit.

3) **Tubular RO Membranes**

Tubular membrane processes operate on much the same principle as the hollow fine fibre, except that the tubes are much larger, on the order of 1.3 mm inside diameter. A helical tubular module is shown in Figure 22. The basic module configuration is a nominal 2.5 cm diameter tubular membrane, wound onto a support spool in a multiple layer helical coil. The membrane is supported by a network of polyester filaments. Composite metal and plastic fittings are attached to each end of the membrane tube and

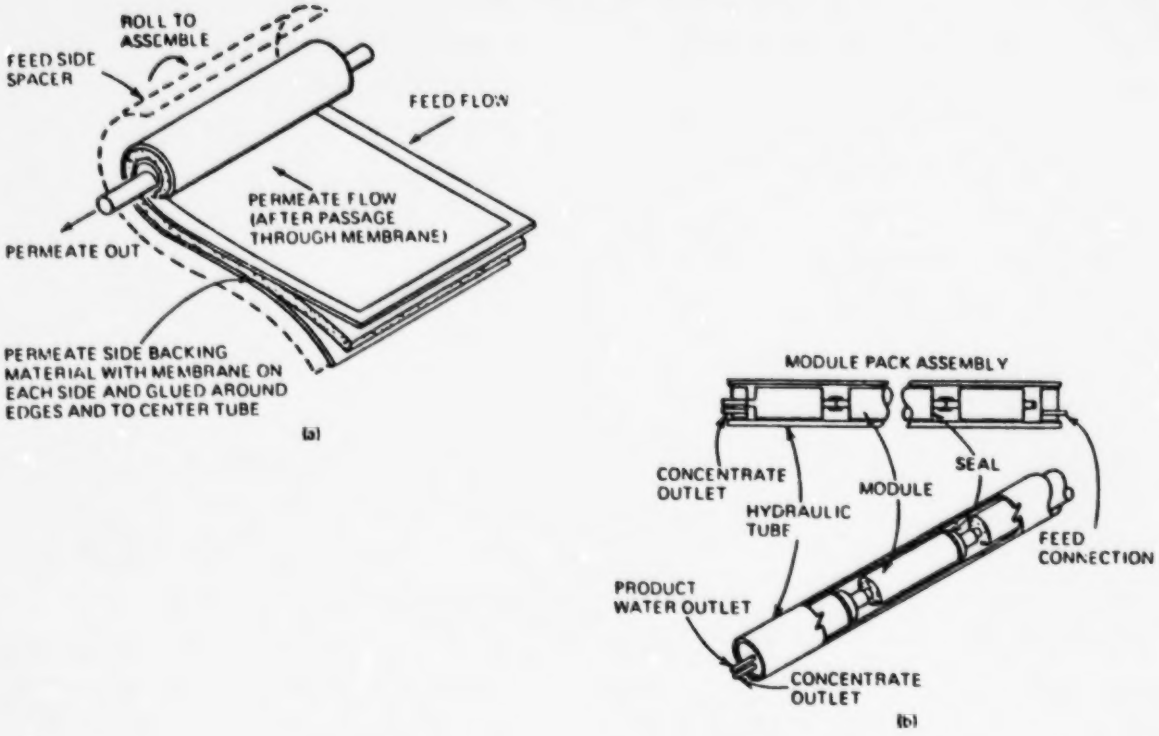


FIGURE 19 SPIRAL WOUND REVERSE OSMOSIS MODULE a) Module; b) Vessel assembly (Courtesy of Fluid Systems Div. UOP, San Diego, CA)

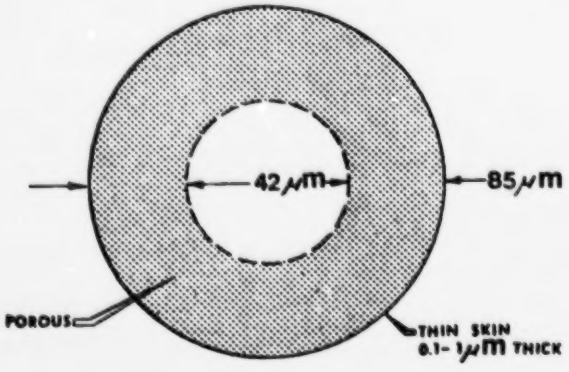


FIGURE 20 HOLLOW FIBRE (asymmetric aromatic polyamide) REVERSE OSMOSIS MEMBRANE AS MANUFACTURED BY DU PONT (transverse section)

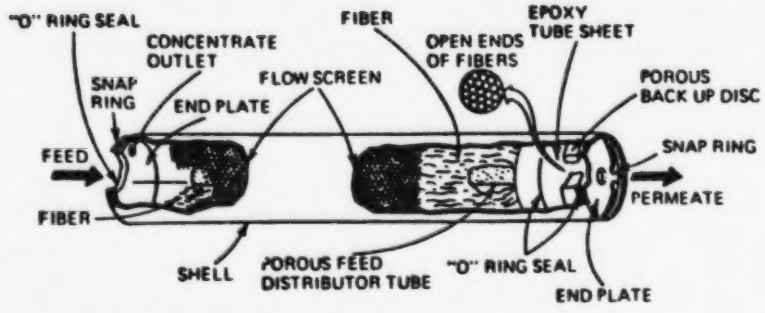


FIGURE 21 HOLLOW FIBRE REVERSE OSMOSIS MODULE AS MANUFACTURED BY DU PONT

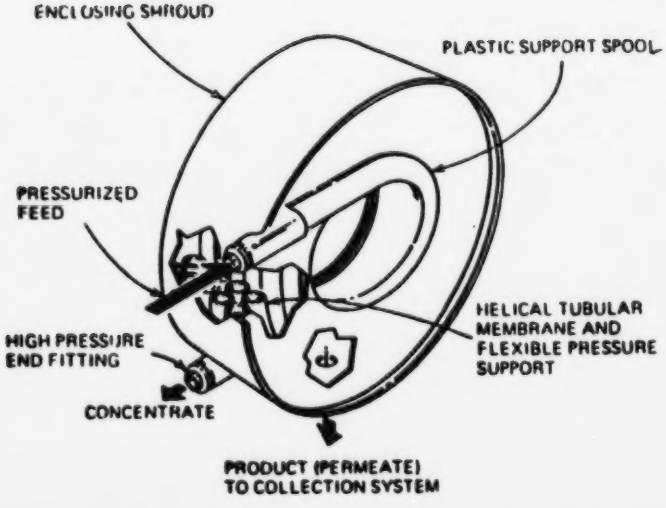


FIGURE 22 PHILCO-FORD HELICAL TUBULAR REVERSE OSMOSIS MODULE

its polyester pressure support. The helical tubular membrane is completely enclosed by a plastic shroud. The shroud is intended to prevent damage to the membrane and provide a means for contamination free product collection.

Many materials have been studied for possible use as membranes for water and wastewater purification. The most widely used membrane developed to date is a modified cellulose acetate film. Reverse Osmosis membranes generally consist of an asymmetric structure which combines a very thin, dense skin on a porous support structure. This combination provides very high solute rejection while permitting relatively high water flow.

The modified cellulose acetate membrane currently in general use is approximately 100 µm thick. It is asymmetric, having on one surface a relatively dense layer, approximately 0.2 µm thick, which serves as the rejecting surface. The remainder of the film is a relatively spongy, porous mass, containing approximately two-thirds water by weight; this portion must be kept wet at all times.

The ability of RO membranes to reject electrolytes increases with an increase of valency. Among cations, calcium and magnesium are rejected to a greater extent than sodium, while for the anions, sulphate is rejected more than chloride. Free gases that tend to diffuse through the membranes fairly easily include carbon dioxide (pH 4), oxygen, sulphur dioxide (pH $\leq$ 3), chlorine (pH 7), and hydrogen sulphide. It appears, therefore, that the basis for rejection is more complicated than that of a simple molecular sieve, but the exact mechanism is still in dispute (Mulligan and Fox, 1976).

For water and wastewater containing mostly higher molecular weight and/or less polar organics (such as humic substances and pesticides), the choice of favourable engineering systems for the reverse osmosis process becomes more important than that of membrane materials (Chian and Fang, 1977).

The majority of non-structural membrane problems resulting in decreased productivity can be categorized into four groups: hydrolysis, degradation, plugging, and fouling. Proper pretreatment can reduce or eliminate these problems (Kasper, 1979).

Plugging refers to the physical blockage or clogging of the membrane surface by particulate matter which reduces permeate flow. Scaling is one form of the more general plugging category in which chemicals precipitate on the membrane surface in contrast to physical straining of particulate matter present in the feedwater. Particulate matter responsible for plugging can be colloidal particles (clay, silica, metal hydroxides) present in the raw feedwater, metals precipitated by oxidation (ferric oxide, manganese dioxide), and species precipitated due to concentration in the brine (calcium sulphate,

silica) (Kasper, 1979). Examples of metal oxide precipitation are the oxidation of soluble ferrous iron to ferric oxide and soluble manganese to manganese dioxide.

The particulate matter in the feedwater is generally quantified in terms of turbidity and/or the rate of filtration through a micropore membrane filter. Concentrations of particulate matter too low for detection by turbidity instruments can be quantified by filtration rate. These filtration rates are reported as plugging factors, fouling indices, or silt density indices. Feedwaters with soluble iron or manganese do not necessarily show the presence of any particulate matter by the turbidity or filtration techniques. The oxidation process forming the solid phase can occur after pretreatment in the membrane module (Kasper, 1979).

Accumulation of particulate matter on the membrane surface can also decrease permeate quality by increasing concentration polarization. The accumulated particulate matter interferes with the hydrodynamics of the brine flow along the membrane surface thereby increasing the stagnant boundary layer responsible for concentration polarization (Kasper, 1979).

A second type of plugging is the precipitation of solid phase which occurs at the downstream end of the module where the feedwater salinity has been concentrated. Typical problem materials are calcium sulphate, calcium carbonate, and silica. Supersaturation under the illustrated conditions occurs only in the concentrated brine. Scaling does not occur in the upstream end of the module where the scalant concentrations are lower (Kasper, 1979).

Fouling by bacterial growths, slimes, or organics may also occur. Fouling is distinguished from plugging in that it is the physical blockage of the brine flow channels and does not necessarily occur on the membrane surfaces. While water continues to flow through the brine channels, the hydrodynamic turbulence minimizing concentration polarization is reduced resulting in poor quality permeate.

Membrane degradation is a general term which refers to any deterioration of the membrane's ability to reject salt and pass permeate. Degradation can be caused by chemical dissolution of the membrane, oxidation of the membrane material, and deterioration of the chemical integrity of the membrane by other phenomena. Hydrolysis, a specific form of degradation, can occur in certain membrane materials such as cellulose acetate. Hydrolysis is distinguished from other types of degradation since it naturally occurs in all cellulose-based membranes. The hydrolysis rate is affected by pH and temperature. In a system with proper pretreatment, temperatures, and pH, hydrolysis

rates of most commercial cellulose acetate membranes are extremely low resulting in useful membrane lives of five to ten years (Kasper, 1979).

Table 11 shows the non-structural problems encountered with reverse osmosis membranes and typical pretreatment required while Table 12 shows the typical pretreatment requirements for three commercial membrane materials.

TABLE 11 GENERAL CATEGORIES OF MATERIAL DETRIMENTAL TO MEMBRANES (Kasper, 1979)

Phenomena/ Material	Membrane Degradation	Hydrolysis	Scaling	Fouling	Typical Pretreatment Process
Physical					
Temperature		X			Cooling Tower
Particulates			X		Coagulation/ Filtration
Chemical					
Precipitation		X	X	X	Softening, Filtration
Oxidants	X				Aeration/ Filtration
Solvents	X				Activated Carbon
pH		X			Acid Addition
Biological					
Bacterial Particulates/Slimes			X	X	Disinfection
Bacterial Enzymes	X				Disinfection

Reverse osmosis has been applied in the treatment of water and wastewater at power plants. Applications include the following water streams:

- chemical cleaning wastes,
- cooling water,

TABLE 12 TYPICAL PRETREATMENT REQUIREMENTS FOR COMMERCIAL MEMBRANE MATERIALS AND MODULE CONFIGURATIONS (Kasper, 1979)

Membrane Material	Cellulose Acetate	Cellulose Triacetate		Polyamide	
Configuration	Spiral	Spiral	HFF	Spiral	HFF
pH Range	4.0 - 7.5	4.0 - 8.0	4.0 - 7.5	4.0 - 11.0	4.0 -11.0
Maximum Temperature (°C)	30	35	35	35	35
Chlorine - Maximum Operating (mg/L)	0.5 - 1.0*	0.5 - 1.0*	1.0	0	0
Turbidity - Maximum JTU	0.5 - 1.0*	0.5 - 1.0*	1.0	1.0	US**
Fouling Index/SDI - Maximum	US**	US**	3	US**	3

* varies depending on temperature and manufacturer
** US - unspecified

- low and medium strength chemical wastes from floor drains,
- laundry wastes,
- electrostatic precipitator washing water,
- flue gas desulphurization makeup water,
- ash recirculating water, and
- feed for brine concentrator.

Cooling tower blowdown is, for the most part, concentrated natural waters, and there is a large data base on the treatment of natural waters. Nevertheless, treatment of cooling tower blowdown can be different in that chemicals may have been added to reduce scaling or corrosion and corrosion products may be present.

Reverse osmosis has been demonstrated to be applicable in treating cooling water for reuse (Chen et al., 1975; Kasarek, 1978).

Chian and Fang (1975) indicated that cellulose acetate and aromatic polyamide membranes satisfatorily removed chemicals from cooling tower blowdown. At 67 percent product recovery, permeates from both membranes contained a smaller amount of

chemicals than those found in municipal water used for the makeup feedwater. A higher product water recovery should be used in practice to an extent limited only by the solubility of calcium sulphate.

TVA conducted a preliminary study on treating cooling tower blowdown by reverse osmosis. One blowdown sample obtained from a steam plant in the southwest was filtered through 1 to 3-μm fibre filters for suspended solids removal, and then the blowdown was tested by four reverse osmosis modules: Du Pont Spiral-Wound Polyamide membrane, Dow Hollow-Fibre Cellulose Triacetate membrane, Roga Spiral-Wound Cellulose Triacetate membrane, and Du Pont Hollow-Fibre Polyamide membrane. The testing results based on 10 percent volume recovery are shown in Table 13 and indicate a high percentage removal of chromium, zinc, and phosphate (commonly used corrosion inhibitors) (Tang et al., 1980).

Another application of reverse osmosis is its use as a preconcentrator of brine in cooling water blowdown prior to treatment by a vapour-compression evaporator. The reverse osmosis system can be designed to concentrate the blowdown by a factor of five thereby reducing the evaporator size by a similar factor (Figure 23).

In another evaluation of technologies for treating cooling water blowdown, a reverse osmosis system was tested at a flow rate of 80 L/s (Houle et al., 1979). The reverse osmosis system consisted of membranes arranged in 4 banks of modules in a 3-stage configuration. The water in this test had been pretreated by the cold lime soda softening process. Table 14 shows the characteristics of the cooling water, pretreated water and results of the reverse osmosis system where 75 percent of the pretreated water going through the reverse osmosis system is recovered. The permeate contains 475 mg/L of total dissolved solids, measured as sum of seven individual ions. Another stream of cooling tower blowdown was also treated by the same reverse osmosis system. This stream did not receive lime in the softening step (Table 14).

Reverse osmosis in comparison to vertical tube evaporation and vapour compression evaporation was found to have a larger ponding requirement for reject brine disposal, was relatively less expensive with its application to cooling tower blowdown, was very sensitive to upsets in the pretreatment plant operation and produced poorer quality water (Houle et al., 1979). Reverse osmosis and its costs are sensitive to the feed composition in comparison to distillation which is not sensitive to moderate changes in feedwater composition (Houle et al., 1979).

It has been shown that reverse osmosis can be used to treat cooling water for discharge or for reuse. Because reverse osmosis permeate is generally of high quality, it

TABLE 13 REVERSE OSMOSIS OF COOLING TOWER BLOWDOWN (Tang et al., 1980)

Membrane Type	Du Pont Spiral Wound		Dow Hollow-Fibre+		Roga Spiral Wound		Du Pont Hollow-Fibre	
Permeate (L/s)	0.03		0.02		0.07		0.10	
Operating Pressure (kPa)	2760		1380		2760		2760	
Analyte*	Feed	Rejection (%)	Feed	Rejection (%)	Feed	Rejection (%)	Feed	Rejection (%)
Total Alkalinity as $CaCO_3$	58.1	84.2	43	90.7	70	91.4	72	86.5
Conductivity µS	4700	82.1	5000	95.6	4100	85.2	8900	89.2
TDS	4000	85.8	4300	95.3	8300	80.7	-	-
CO	24	95.8	19	89.5	21	33.3	35	94.3
Chromium	0.01	>80	0.01	>80	0.01	>80	0.01	>80
Zinc	0.2	85	0.25	92	0.37	83.8	0.89	96.6
Total Phosphorus	0.49	93.9	0.67	98.5	1.34	96.3	1.74	97.1
Kjeldahl Nitrogen	0.95	78.9	0.78	48.7	0.45	71.1	0.55	97.3
Nitrate (NO_2NO_3)	17	80	18	87.2	27	64.8	55	84.5
pH (units)	6.3	-	6.3	-	6.5	-	6.4	-

+ specially designed for testing purposes

Note: * all analyses expressed in mg/L except when indicated otherwise
feed rate for all modules was 0.25 L/s

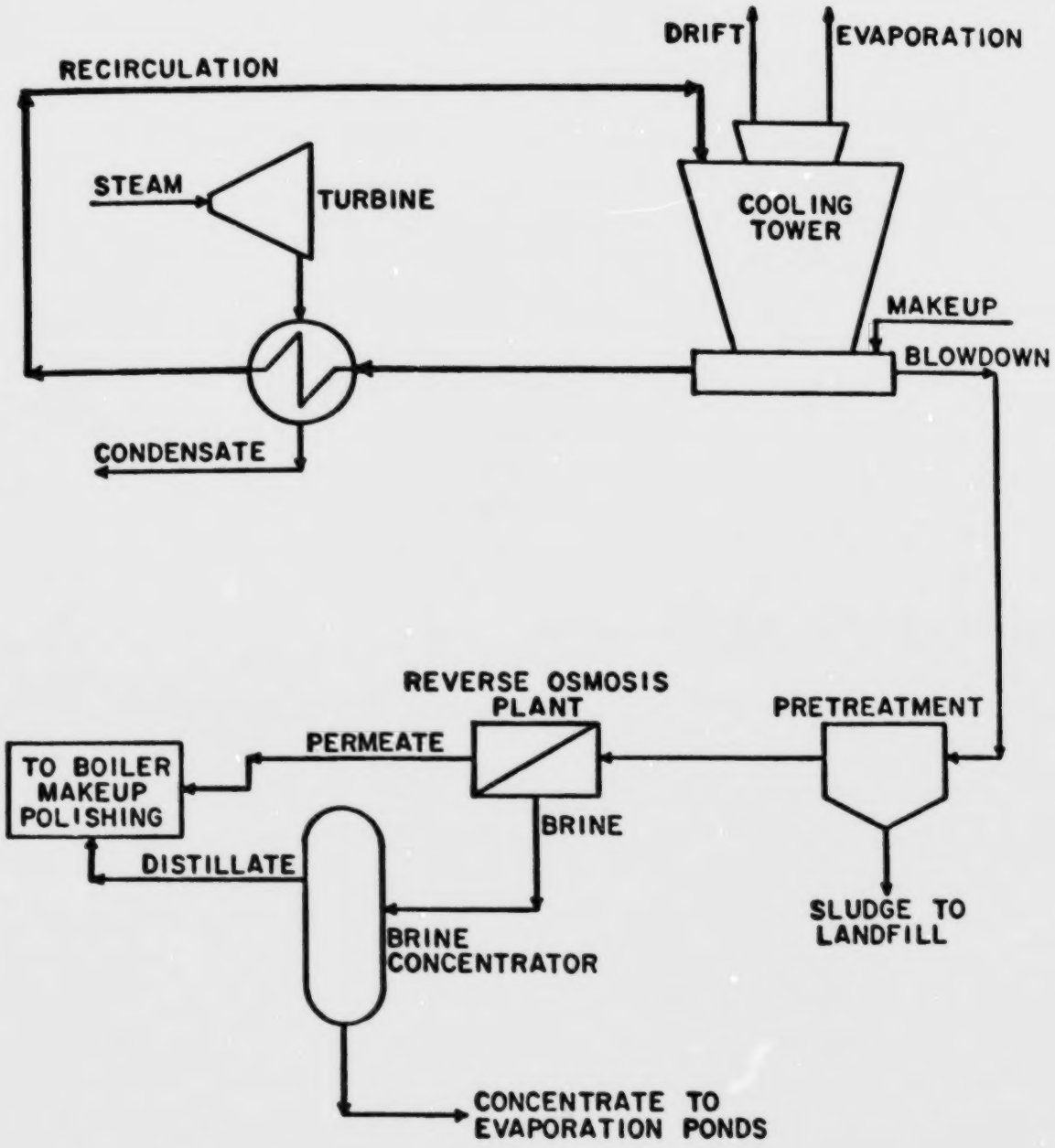


FIGURE 23 FLOW DIAGRAM FOR COOLING TOWER BLOWDOWN TREATMENT BY REVERSE OSMOSIS FOR REUSE (Tang et al., 1980)

TABLE 14 TREATMENT OF COOLING TOWER BLOWDOWN BY REVERSE OSMOSIS WITH AND WITHOUT LIME SOFTENING (Houle et al., 1979)

Analyte	Cooling Tower Blowdown	Pretreated Blowdown	Reverse Osmosis Permeate	Reverse Osmosis Reject
With Lime Softening				
Na	1320	2018	121	7 708
Ca	400	50	4	187
Mg	400	236	17	893
Cl	208	208	15	786
SO_4	5000	5027	306	19 083
HCO_3	44	43	4	73
SiO_2	150	37	8	125
TDS (sum of ions)	7522	7619	475	28 855
pH (units)	7.3	6.0	5.2	6.3
Temp. (°C)	27	27	27	27
Without Lime Softening				
Na	710	1265	126	4 696
Ca	533	50	0	200
Mg	193	174	0	700
Cl	266	266	36	956
SO_4	3820	3847	214	14 638
HCO_3	35	43	7	151
SiO_2	5	5	1	17
TDS	5562	5650	384	21 358
pH (units)	6.7	6.0	5.2	6.3
Temp. (°C)	27	27	27	27

Note: all analyses expressed in mg/L except where noted

would usually be reused. The brine, however, is more concentrated than the feed and often must be stored indefinitely or disposed of at high cost. If this is the case, overall cost is reduced by concentrating the brine as much as possible to reduce its volume (LeGros et al., 1970).

Brine concentration by reverse osmosis is usually limited first by calcium sulphate deposition and then by osmotic pressure increases. To minimize the blowdown flow, cooling water will usually be concentrated to the maximum extent possible without the precipitation of scale. Whatever the potential scale forming species may be, further concentration in the reverse osmosis process will lead to scaling of the membranes unless precautions are taken.

Feed treatment is essential to reduce the concentration of scale formers so that their solubilities are not exceeded in the reject stream and in particular, to the boundary layer between reject brine and membrane where the concentrations are maximum. For example, if the recovery of purified water is 75 percent, the reject stream represents one quarter of the original volume at roughly four times the concentration. Process design would require:

- the reduction of calcium concentration to a value that avoids $CaSO_4$ scale formation in the reject stream;
- the precipitation of Mg as a hydroxide to remove sufficient SiO_2 to prevent silica scaling in the reverse osmosis modules; and
- the adjustment of the pH of the softener water to ensure the pH is below the Langelier Index for $CaCO_3$ precipitation in the reject stream (Houle et al., 1979).

Osmotic pressure also limits water recovery. System pressure must substantially exceed the osmostic pressure in order to maintain practical permeate productivity rates. Reverse osmosis modules designed for brackish water desalting are limited to operating pressure below 2760 to 4140 kPa, depending on the module; and practical brine concentrations are typically 15 000 to 20 000 mg/L. Higher concentrations, up to about 790 000 mg/L, are feasible in modules designed for seawater desalting (Tang et al., 1980).

Finally, in selecting a reverse osmosis system for treating cooling water, the temperature tolerance of the membranes should be carefully checked against expected water temperatures. Some type of auxiliary cooling may be necessary as pretreatment to the reverse osmosis unit.

Laboratory tests were conducted on a once-through ash pond effluent by the TVA (Tang et al., 1980). Fly ash pond effluent tested was acidic and contained high concentrations of several trace metals.

The major constituents in the ash pond effluent were suspended solids, sulphate, calcium, magnesium, and silica; therefore, spiral-wound and tubular modules were selected to treat this wastewater. The fly ash pond effluent was passed through the Roga spiral-wound cellulose triacetate membrane, the Du Pont spiral-wound polyamide membrane, and the UOP Fluid Science tubular cellulose acetate membrane individually. The data on rejection of total dissolved solids from each module are shown in Table 15. The Roga spiral-wound module appeared to be better for treating this type of wastewater, and additional experiments were conducted with this module to treat fly ash pond effluent which had been concentrated by a factor of 1.7 (Tang et al., 1980).

There is no information in the literature on the treatment of coal pile drainage by any membrane process. However, research has been conducted since 1966 on the application of reverse osmosis to acid mine drainage which in some cases is similar to coal pile drainage.

Blackshaw and Pappano (1975) reported on a study concerning the technical and economic feasibility of using reverse osmosis for treatment and purification of acid mine drainage. The reverse osmosis unit was rated at 2.6 L/s product water output, featuring feedflow and waste brine flow controllers that can be pre-set to desired flow rates, depending on recovery requirements and reverse osmosis modular-tube arrays. Wilmoth and Scott (1976) investigated an application of reverse osmosis to a ferrous-iron acid mine drainage in Mocanaqua, PA.

The U.S. EPA (1973) tested spiral-wound reverse osmosis systems on acid mine drainage discharges at four locations: Norton, WV; Morgantown, WV; Ebensbury, PA; and Mocanaqua, PA. The water quality characteristics of those sites were quite different. At all sites, the limiting factor in high recovery operation was calcium sulphate insolubility. Neutralization of the product water was needed to elevate pH in all cases, and to remove residual iron and manganese in some cases. Neutrolosis, which is the blending of neutralized brine supernatant from the reverse osmosis unit back into the feed to the unit, was shown to be a promising process for obtaining maximum recoveries and reducing the brine disposal problem. The pretreatment at all sites consisted of 10 μm filtration. Ultraviolet disinfection, acid injection, or both were needed at some sites to prevent iron oxidation and precipitation.

TABLE 15 RESULTS OF REVERSE OSMOSIS STUDIES OF FLY ASH POND EFFLUENT (Tang et al., 1980)

Membrane+	Feed Composition*	Permeate (L/s)	Rejection (%)
Du Pont Spiral Wound	Conductivity, 840 (μS/cm) pH 4.5	0.03	92.6
UOP Fluid Science Tubular	Conductivity, 827.5 (μS/cm) pH 4.3	0.01	79.3
Roga Spiral Wound	Conductivity, 852.5 (μS/cm) pH 4.3	0.08	93
Roga Spiral Wound	Conductivity, 1450 (μS/cm)	0.07	-
	TDS 1500	0.07	96.7
	Al 9.6	0.07	95.8
	Ca 280	0.07	96.8
	Cd 0.29	0.07	97.9
	Cr 0.25	0.07	93.2
	Cu 6.9	0.07	96.2
	Fe 0.56	0.07	> 91
	Pb 0.042	0.07	> 90
	Mg 51	0.07	96.5
	Mn 1.5	0.07	96
	Se 0.003	0.07	> 90
	Si 27.8	0.07	88.5
	SO_4 815	0.07	96.9
	Zn 6.65	0.07	99.1
	pH 4.7	0.07	-

Note: + operating pressure during testing was 2760 kPa at a flowrate of 0.25 L/s
* all feed composition results expressed in mg/L except where noted

Kaup (1973) proposed a combined treatment process with reverse osmosis and ion exchange for acid mine drainage. After pretreatment for fouling control, 75 percent of the wastewater was recovered by reverse osmosis, and the remaining 25 percent concentrate was treatment by ion exchange.

Table 16 shows the results of an application of reverse osmosis to a ferrous-iron acid mine drainage from Mocanagua, PA (Kaup, 1973). The efficiency of reverse

TABLE 16 RESULTS OF REVERSE OSMOSIS TREATMENT OF ACID MINE DRAINAGE (Kaup, 1973)

	Raw Feed	Waste Brine	Effluent
Conductivity (μS/cm)	1000	3600	17
Acidity as $CaCO_3$	240	810	32
pH (unit)	3.4	2.9	4.5
Ca	130	490	0.5
Mg	90	310	0.6
Total Iron	77	330	0.5
Total Fe^{2+}	64	250	0.5
Na	-	-	-
Al	12	44	0.2
Mn	12	24	0.08
SO_4	750	2800	2.2
Alkaline as $CaCO_3$	0	0	0
TDS	1300	4500	5

Note: all analyses reported as mg/L except where noted

osmosis in removing metals is clearly illustrated in these results. A suggested flow configuration for the use of reverse osmosis to treat coal pile drainage is shown in Figure 24.

Periodic cleaning of metal surfaces in boilers generates a type of waste that contains high TDS (100 to 5400 mg/L), copper (100 to 600 mg/L) and other metal concentrations (Tang et al., 1980). Treatment of these cleaning wastes is generally accomplished by conventional chemical precipitation processes; however, some of the metal ions, especially copper, are difficult to precipitate out due to their complex forms.

In a series of laboratory tests conducted by the TVA, five types of reverse osmosis membranes were evaluated for the treatment of alkaline phase drain cleaning waste following chemical precipitation and ultrafiltration (Table 17). Membrane fouling problems resulting from the copper precipitates in the unstable cleaning waste were considered a possible key factor preventing the operation at the high volume recovery. However, the membrane processes were still considered practicable if a simple and inexpensive pretreatment process could be found for this waste.

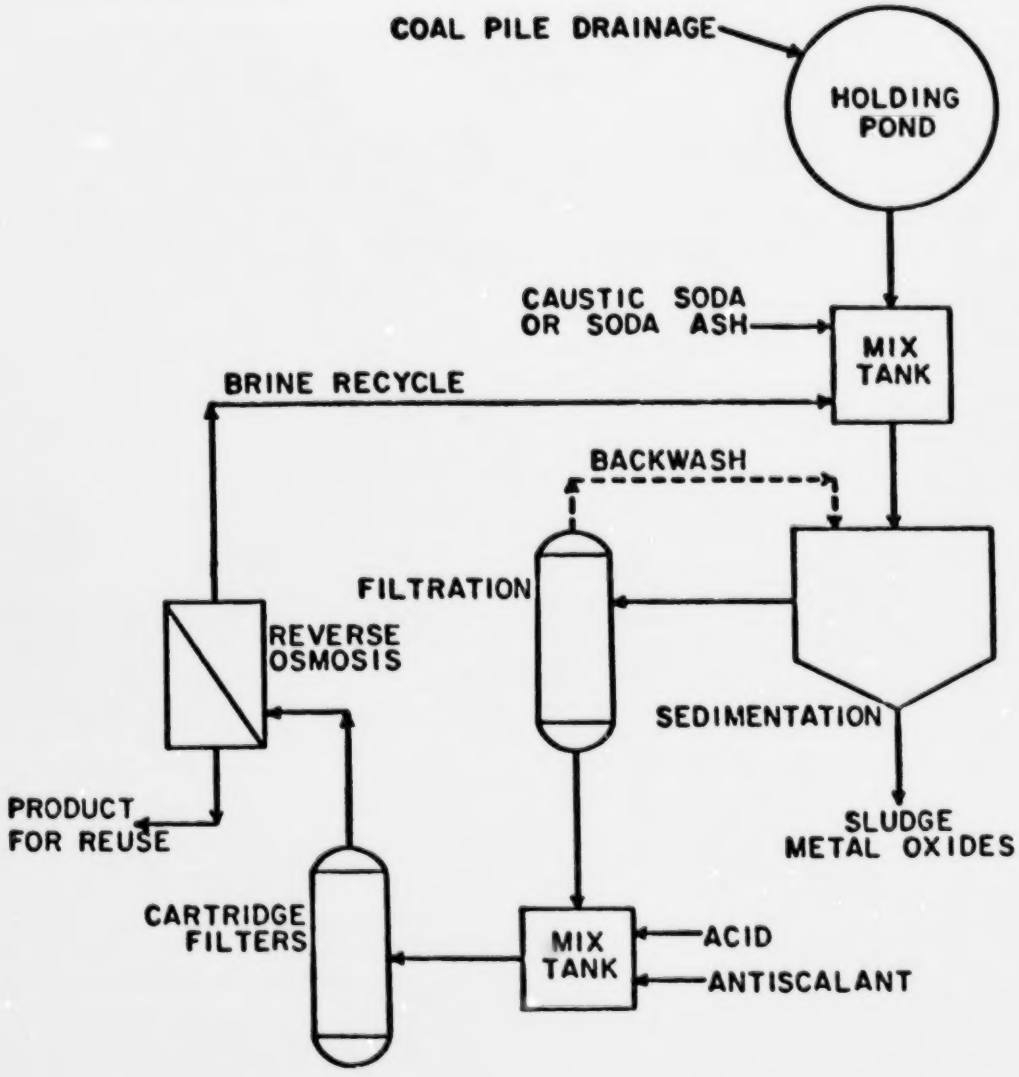


FIGURE 24 CONFIGURATION OF A REVERSE OSMOSIS TREATMENT SYSTEM FOR COAL PILE DRAINAGE (Tang et al., 1980)

TABLE 17 RESULTS OF REVERSE OSMOSIS TREATMENT ON CHEMICAL CLEANING WASTES (Tang et al., 1980)

Membrane Type	Feed Composition*	Rejection (%)	Flux L/s	Pressure (kPa)	Feedflow L/s
Du Pont Hollow-Fibre	Alkaline copper waste				
	Cu 2200	99.9			
	NH_3-N 10 500	20.4	0.05	2410	0.27
	TDS 4500	95.8			
	pH 11.1	-			
Du Pont Spiral Wound	Alkaline copper waste				
	Cu 1700	98.8			
	NH_3-N 9450	40.7	0.02	2760	0.24
	TDS 4300	87.4			
	pH 10.0	-			
Roga Spiral Wound	Neutralized copper waste				
	Cu 820	83.6			
	NH_3-N 4100	58.8	0.02	2760	0.26
	TDS 2600	79.0			
	pH 4.35	-			
UOP Fluid Science Tubular	Neutralized copper waste				
	Cu 2000	78.5	0.004	3790	0.24
	pH 4.0	-			
Dow Hollow-Fibre	Neutralized copper waste				
	Cu 410	75.0	0.0006	1380	0.26
	pH 4.0				

Note: a rejection = 1 - (concentration in permeate)/(concentration in feed)
* all analyses expressed in mg/L except pH (units)

In 1974, a 158 L/s spiral-wound module reverse osmosis system was tested at the H Power Station of Karaso Electric Power Company in Japan to treat plant wastewater for reuse. These included electrostatic precipitator wash and oily waste. It was concluded that following coagulation and filtration pretreatment, reverse osmosis was extremely reliable (Kakimoto et al., 1975).

5.3.2 Ultrafiltration Technology. The ultrafiltration membrane process separates colloidal materials and high molecular weight solutes such as microorganisms, polymers and clays. Ultrafiltration is similar to reverse osmosis as the driving force is pressure. Membranes are made from similar materials and the arrangement of the feed permeate and rejection streams is the same. It differs from reverse osmosis by being unable to separate dissolved inorganic salts, uses a more porous membranes and operates under lower pressure.

Since ultrafiltration is used to separate high molecular weight solids, fouling of the membrane can be expected. The physical configuration of the membrane, therefore, is selected to facilitate easy cleaning. Tubular configurations are used where fouling is expected. High fluid velocities and large diameter tubes (up to 25 cm) are used to promote water turbulence and scour membrane walls. Tubular configurations also facilitate mechanical cleaning.

Spiral-wound ultrafiltration units are somewhat more vulnerable to fouling. Where fouling can be controlled by chemical cleaning or flushing, a significant cost savings is provided. Hollow fibre configurations are generally most vulnerable to fouling.

When fouling is expected, some method of chemical cleaning is planned in addition to mechanical flushing or backwashing. This usually requires pilot-scale testing to verify that the membrane selected can withstand repeated cleanings. Both polisulphane and zirconium oxide membranes can tolerate high temperatures and strong chemicals.

Pressures of 140 to 800 kPa are typical for ultrafiltration systems in contrast to the pressures used with reverse osmosis which are from 2800 to 8400 kPa.

Ultrafiltration is best applied in systems where colloidal and high molecular weight organic solutes must be removed from water and where high rejection of ionic or low molecular weight organics is not required. Industrial applications include treatment of electroplating wastes, water separation and chemical recovery.

Very limited data has been reported on the application of ultrafiltration to wastewaters or process waters from coal-fired steam electric generating stations. The

use of this process has been most often reported as part of the boiler feedwater preparation process.

The performance of ultrafiltration modules in the treatment of boiler cleaning wastes was reported by Tang et al. (1980). Following extensive pretreatment, the boiler cleaning waste was polished for the removal of suspended solids using ultrafiltration. The suspended solids concentration in the permeate was independent of the ratio of volume of permeate to initial volume of feed. Results of this testing are shown in Table 18.

TABLE 18 PERFORMANCE OF ULTRAFILTRATION MODULE* IN POLISHING SUSPENDED SOLIDS FROM THE PRETREATED BOILER CLEANING WASTES (Tang et al., 1980)

	Suspended Solids Concentration (mg/L)	
Volume Recovery+	Feed	Permeate
0.02	6	2
0.5	9	2
0.95	57	3

+ V_P/V_F, where V_P = volume of permeate and V_F = initial volume of feed solution
* Union Carbide 2NJR ultrafiltration modules

5.3.3 Electrodialysis Technology. The electrodialysis separation process is achieved when a direct current electrical voltage is applied across semi-permeable membranes to drive the anions toward the positive electrode and cations toward the negative electrode. Membranes that are selective to passage of anions only or cations only are placed alternatively between the cathode and anode. Ions entering one compartment through a selective membrane cannot escape because they are stopped by the second membrane. This process results in the formation of two compartments, one depleted of ions and the other concentrated in ions. The electrodialysis demineralization process is shown in Figure 25.

There are three different physical configurations used for electrodialysis; the unit cell configuration and two plate and frame configurations, one using sheet flow and the other using a tortuous flow path.

Solutions can become depleted in the boundary layer when the diffusion of ions from the bulk solution does not meet the demand of the ion flow through the membrane.

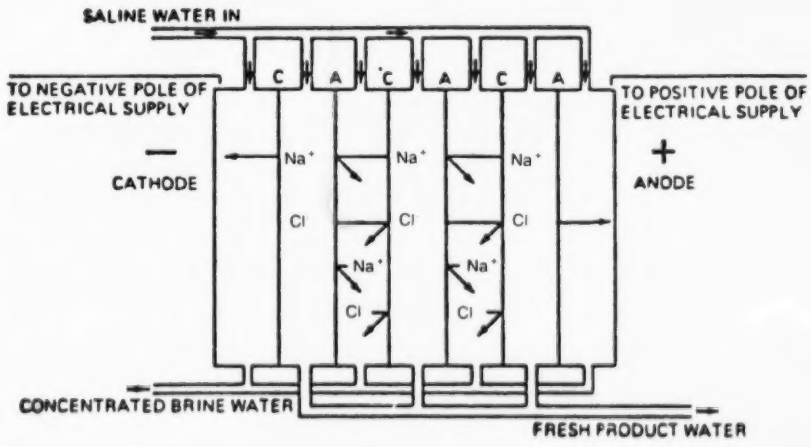


FIGURE 25 ELECTRODIALYSIS DEMINERALIZATION PROCESS

This usually occurs first at the anion membrane and results in the electrodialysis of water. Current is then wasted in transporting OH^- and H^- ions. A key parameter in designing an electrodialysis system is the limiting current density at which disassociation begins to occur. This is a function of the particular solute as well as the physical arrangement and flowrate.

Most electrodialysis membranes permit operation up to 50°C while their ability to withstand extremes in pH vary considerably depending on the manufacturer. Almost all membranes are sensitive to oxidizing solutions.

In addition to scaling caused by exceeding solubility limits, fouling due to the accumulation of suspended solids must be avoided. Suspended solids removal down to 50 to 100 µm is usually required. In addition, iron and manganese are often limited to 0.2 mg/L. The presence of trivalent ions such as aluminum and phosphate may increase

electrical resistance. Although microorganisms do not attack the membranes, they can form an interferring slime layer which would necessitate periodic cleaning (Mulligan and Fox, 1976).

The application of electrodialysis for the treatment of cooling tower blowdown has been demonstrated (Kasper, 1979). A study by Blackburn (1977) indicated that at salt removal rates and concentration ranges applicable to power plant cooling towers, electrodialysis is one of the most cost effective processes. For waters with a TDS of less than 10 000 mg/L, this data shows that electrodialysis is much less expensive than evaporative brine concentrators. Figure 26 shows the configuration of a system to treat cooling tower blowdown by sidestream softening and electrodialysis (Jordan et al., 1976).

Westbrook and Wirth (1976) also described the use of electrodialysis for the treatment of cooling tower blowdown. The overall salt balance in an evaporative cooling tower system could be managed using sidestream softening in combination with electrodialysis. This configuration would reduce the potential for sodium leakage problems such as excessive condensate polishing regeneration and a turbine fouling (Gloodstine, 1974).

The major advantage of electrodialysis over reverse osmosis is that it is able to produce brine concentrations of 8 to 16 percent which are greater than those produced by reverse osmosis (Connelley, 1976).

It has also been suggested that electrodialysis could be used for the regeneration of SO_2 scrubber liquor (McRae, 1977; Grant and Schepers, 1978; Meliere et al., 1974). Although several configurations exist, in general an alkaline-sulphate-sulphite solution is split into separate alkaline and sulphuric acid streams. The alkaline stream is then reused to absorb additional sulphur oxides. Sulphuric acid or SO_2 is recovered for other uses. A three-chamber electrodialysis unit is used. Feedwater enters in the centre and cations such as sodium migrate to the cathode compartment, passing through a cation exchange membrane. At the cathode, cations join with hydroxide ions (OH^-) formed by electrolysis of water. Likewise, anions, such as sulphate and sulphite, pass through the anion membrane where they join with hydrogen ions (H^+) produced by the dissociation of water molecules at the anode.

5.3.4 Summary of Membrane Technologies. A brief review of membrane processes for the removal of dissolved solids, particularly in wastewaters from coal-fired steam electric generating stations is presented in this section. Reverse osmosis, electrodialysis, and ultrafiltation are relatively new process technologies. Based on the literature,

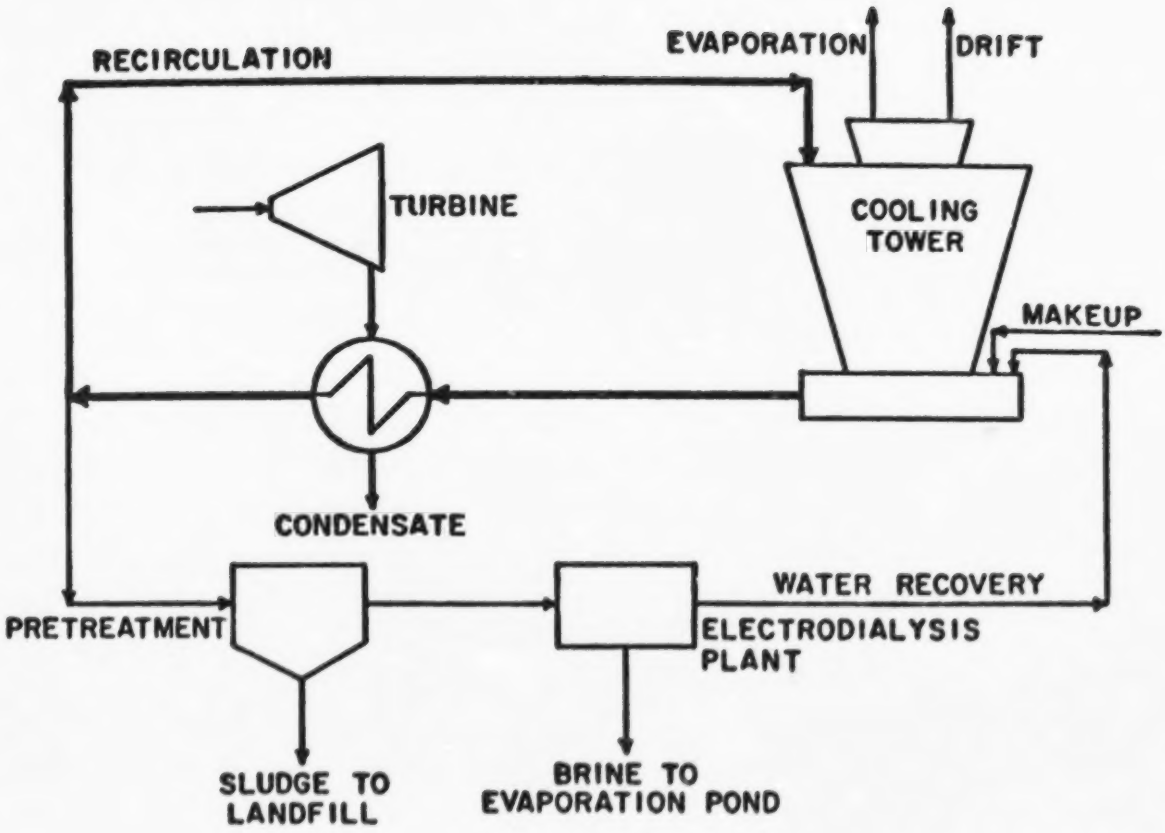


FIGURE 26 FLOW DIAGRAM FOR COOLING TOWER SIDESTREAM SOFTENING AND DESALTING WITH ELECTRODIALYSIS (Jordan et al., 1976)

reverse osmosis is the most widely utilized process used for the treatment of dissolved solids in wastewaters.

Membrane technologies are not suitable for removing materials which are unstable and likely to precipitate as they are concentrated. These materials will foul membranes and should be removed by conventional techniques if possible. It is inappropriate, therefore, to consider membrane technology without extensive pretreatment or as a method for preventing scale deposition (Tang et al., 1980).

With proper pretreatment, reverse osmosis and electrodialysis can be used to remove and concentrate dissolved salts from various streams. In this role, membrane technology must compete with distillation. Distillation is typically more expensive but requires less extensive pretreatment than reverse osmosis or electrodialysis. Electrodialysis is estimated to be least expensive but does not produce product water of comparable quality to either reverse osmosis or distillation.

In considering electrodialysis, reverse osmosis, or distillation for removing dissolved solids, the need for dissolved solids control should be critically examined. When the need is established, membrane technology should be considered as a viable alternative to distillation. Closed-loop systems to which this concept could be applied include cooling systems, ash sluice systems, and SO_2 scrubber systems.

When heavy metals cannot be satisfactorily removed by pH adjustment, precipitation, adsorption, and suspended solids removal, reverse osmosis should be considered as a polishing step. Brine may be recycled to the precipitation step. This concept may be applicable to coal pile drainage and chemical cleaning wastes. Ultrafiltration has been proving competitive in treating oily wastes and as a pretreatment for reverse osmosis.

While reverse osmosis systems design is not an exact science, certain classes of problems can be handled in a straight-forward manner. This includes processing solutions of inorganic ions to concentrate or purify, providing that adequate pretreatment is available. Pilot testing of the pretreatment step is advisable, but pilot testing of the reverse osmosis system is not generally necessary. Exceptions include situations where adequate pretreatment is not practical and where organic solutes or weakly ionized species are important.

Reverse osmosis is an acceptable process for removing inorganic and organic priority pollutants. Electrodialysis is feasible for removing only inorganic priority pollutants. Ultrafiltration holds no promise for removing US EPA priority pollutants from wastewaters.

5.4 Brine Disposal

A brine disposal system must be capable of either permanently containing the wastewater contaminants or removing the non-desirable components from the wastewater. In areas of net precipitation, evaporation ponds cannot be utilized for permanent containment and waste disposal. In these cases, a drying process can be used to produce a dry solid waste for permanent disposal in a secure landfill.

5.4.1 Spray Driers. The two mechanisms involved in drying are heat transfer and mass transfer. Heat must be supplied to the material in order to vapourize the liquid and the resulting vapour must be carried away by some means such as an air stream or vacuum. Heat must also be transferred from the drying gas or hot surface to the centre of the material or to the point in the material furthest from the source of heat. The rate at which this heat transfer occurs varies inversely with the distance between the heat source and the material. The rate also varies with the area exposed to the heat source, the amount of agitation in the material and turbulance in the heating gas (Sloan et al., 1967). Five factors govern the speed of drying:

1) Moisture Dispersion: Rapid drying requires the maximum possible exposure of most surface; the drying of suspended particles, therefore, is more rapid than a cake of material.

2) Temperature Differential: The rate of drying is roughly proportional to the temperature difference between the heating medium and the material being dried.

3) Agitation: Fast drying is promoted by rapid movement of the material and drying medium.

4) Particle Size: During drying, moisture from the interior of a particle diffuses to the surface where it evaporates from the surface. This transfer will occur most quickly with small particles.

5) Particle Structure: Since moisture must reach the particle surface to be evaporated, particles with pores or interstices dry more readily (Sloan et al., 1967).

Spray driers are most frequently used for solutions or slurries. In this process, the rate of moisture removal from the wet material is directly proportional to:

- three halves power of the particle diameter ($d^{3/2}$);
- difference in temperature between the hot gas and the particles;
- square root of the mass velocity of the drying gas;
- film coefficient for heat transfer for the drying gas; and
- pressure.

Typically, the drier consists of a large cylindrical, vertical chamber into which the material to be dried is sprayed as droplets by atomizer nozzles (Figure 27). Hot gas is fed into the chamber to supply the required heat of evaporation. Water rapidly

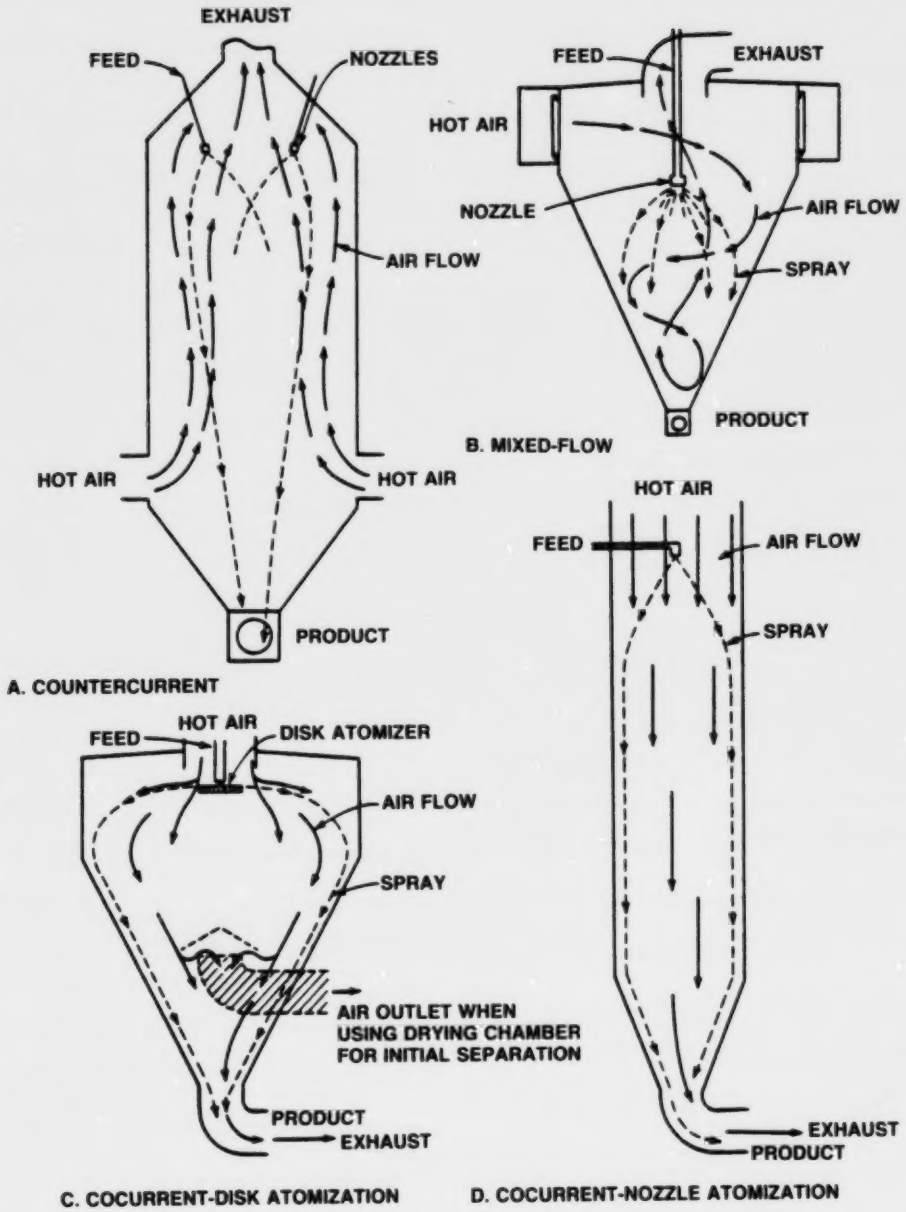


FIGURE 27 SPRAY DRIER CONFIGURATIONS (Sloan et al., 1967)

evaporates leaving behind dry solids which are removed from the gas stream. Table 19 shows the operating characteristics of two sizes of spray driers. The actual systems size would depend on site-specific factors such as required throughput. Spray drier systems are available with capacities of about 3 to 120 L/min.

TABLE 19 OPERATING CHARACTERISTICS OF SMALL AND LARGE SPRAY DRIERS (Sloan et al., 1967)

	Small Drier		Large Drier	
Parameter	Typical	High	Typical	High
Operating Temperature (°C)	260	540	260	540
Evaporative Capacity (kg H_2O/min)	180	450	3 000	7 260
Heat Requirement (MJ/min)	1 270	2 320	21 100	36 900
Power Requirement (kW)	15	22	164	209

A spray drier is currently being used at the Gainesville Regional Utilities, Deerhaven Power Station. This generating station is located near Gainesville, in north-central Florida, where there is a net positive annual evaporation rate which precludes the use of brine evaporation lagoons. At this station, brine produced by a brine concentrator is spray-dried and the resulting salts are disposed of in a secure landfill.

5.4.2 Single/Multi Stage Lagoon. Brines generated from a variety of industrial processes have been stored or disposed of in evaporation lagoons. The pond configuration and use depends on a variety of factors such as wastewater chemistry and land availability. Two inherent disadvantages associated with pond disposal are potential contamination of groundwater and inhibited mineral recovery due to slow salt deposition rates.

Arid regions with high evaporation rates are more conducive to single-stage evaporation lagoons than more humid areas. Evaporation equals or exceeds precipitation on an annual basis in very few regions of Canada. Only in these areas could a lagoon system be considered for brine disposal. The annual evaporation rate is not constant at any particular location, but is influenced, among other things, by the height of the berm above the liquid level. Lagoons are usually shallow in an attempt to provide optimum

evaporation rates (Morrison et al., 1977; Mercado, 1975). The usual depth of ponds is usually limited to about 3 metres.

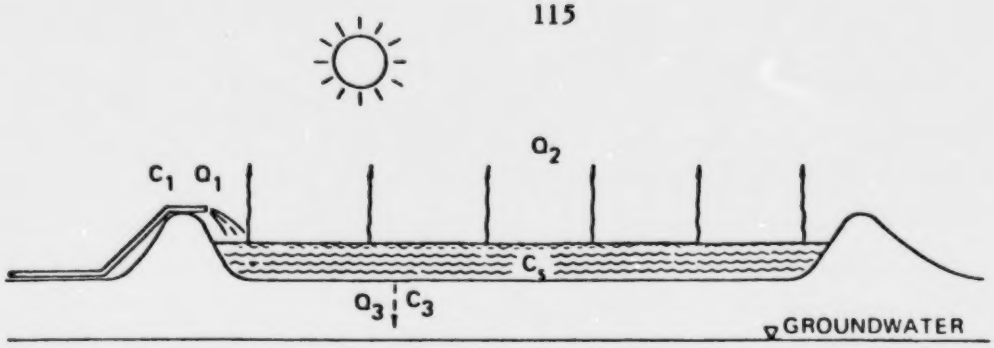
Most designs of single-stage disposal lagoons include the provision of either a natural or synthetic liner. Liners are used to prevent potential groundwater degradation by contamination from the stored brine. The selection depends on the chemical characteristics of the confined brine, lifetime requirements and economics. The characteristics of various pond liners have been discussed in several studies (Princiotta, 1974; Rossoff and Rossi, 1974). Synthetic membranes, although theoretically superior have become subject to question concerning their ability to contain wastewaters for extended periods (Haxo, 1975; Geswein, 1975). Solid materials such as clay impede but do not prevent the seepage of wastewater from the pond when used as liners. Their use is then to control leakage rather than absolute containment.

Figure 28 shows a mass balance around a single-stage evaporation pond. Groundwater contamination results from the Q_3 and C_3, component of the balance. Because of the large area of an evaporation pond, the entire pond bottom theoretically represents a potential pathway for the transport of contaminants to the groundwater. It is evident why the need for a liner system is so great. In the case of soil material liners, erosion increases with time as does the salt concentration (Morrison and Weaver, 1978). In this way, the potential leachates with high concentration increases as the liner integrity decreases with time. This trend would continue throughout the life of the pond until abandonment or mineral recovery occurs.

Single-stage evaporation ponds are usually not conducive to mineral recovery. Relatively large pond sizes which are required for optimal evaporation rates result in the deposition of recoverable minerals over a large area. To consider mineral deposit recovery, the deposit must be about a metre in depth to be economically feasible (Morrison and Weaver, 1978). The time required for evaporation may be long; therefore the period before minimal recovery would also be long which in turn could be a long-term hazard to groundwater.

Multi-stage lagoon operation involves the practice of transferring water from one pond to another, thereby increasing salinities until the majority of the salts finally precipitate in the final pond. This technique is used primarily for salt recovery by a number of commercial salt companies and may be applicable for brine disposal.

Figure 29 shows a radial and square configuration for multi-stage lagoons. As the water is transferred from one basin to the next, the salts gradually concentrate by evaporation. The hypersaline water reaches the last pond where the solubility product is



Q_1 = QUANTITY OF FLUIDS INTO THE POND

C_1 = CONCENTRATION OF SALTS

Q_2 = EVAPORATION; f (WEATHER, SURFACE AREA, PARTIAL PORE PRESSURE, ETC.)

Q_3 = $AK\Delta H$ (Total Downward Flux)

A = AREA

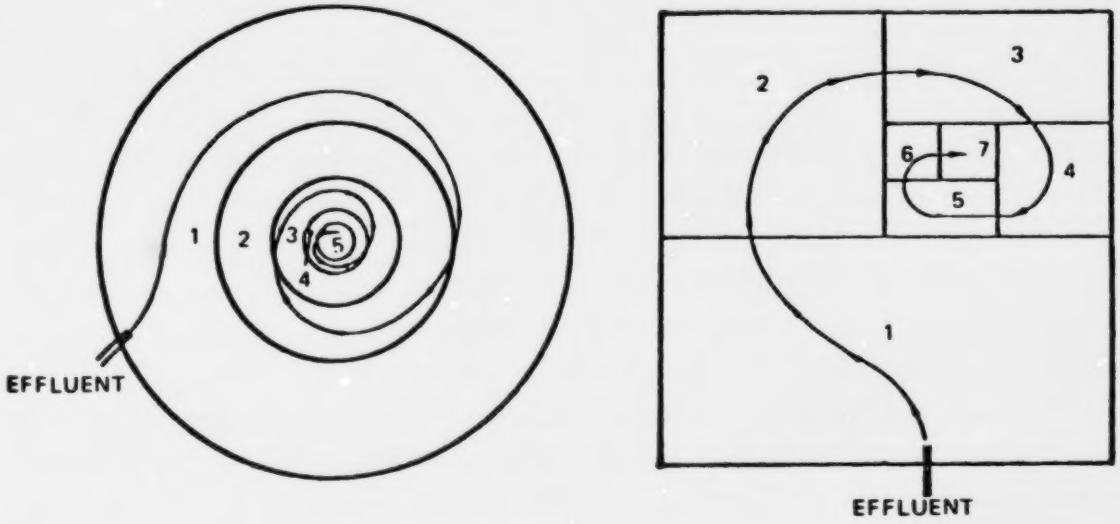
K = COEFFICIENT OF PERMEABILITY

H = HYDRAULIC HEAD

C_s = SATURATION CONCENTRATION

C_3 = QUANTITY OF SALTS LEAVING THE POND

FIGURE 28 MASS BALANCE FOR SINGLE-STAGE POND (Morrison and Weaver, 1978)



A. RADIAL CONFIGURATION (5 STEPS)

B. SQUARE CONFIGURATION (7 STEPS)

FIGURE 29 MULTI-STAGE LAGOON CONFIGURATIONS (Morrison and Weaver, 1978)

exceeded and the salts precipitate out. In this way the smallest pond in the final stage contains the highest salt concentration. Also, the brines with the highest potential for groundwater contamination are present in the smallest basin. Mineral recovery is more likely since the salt deposit is deeper and deposition occurs more quickly.

In single-stage ponds the salts concentration will reduce the vapour pressure of the brine which in turn reduces evaporation. This follows Raoult's Law which states that lowering of the vapour pressure of a solution is equal to the mole fraction of the solute in solution (Glasstone and Lewis, 1960). The advantage of multi-stage lagoons is that when brines are transferred from one stage to another after a specific salt concentration is attained, higher evaporation rates are possible for a larger area of water when compared to hypersaline brines in a single-stage system. In multi-stage lagoons, only the final smallest pond will contain significantly higher salt concentration which would reduce evaporation losses.

Given that sufficient suitable land is available and climatic conditions permit, natural evaporation single-stage lagoon disposal of brine may represent the least costly brine diposal method. However, the situation may change greatly if the cost of providing a satisfactory low permeability pond lining must be considered. Studies completed on the zero-discharge requirements in the power industry in the western U.S. have shown that unless there is a natural low permeability geological formation that favours low cost evaporation pond constituents, processes to concentrate the salt and return water to plants for consumption use are the most economical method (Heist, 1981). Additionally, the integrity of many liner materials with soil material or membrane have not yet been conclusively demonstrated over time.

The utilization of evaporation ponds is seemingly quite simple, however, reports based on operating experience indicate the contrary (Anon., 1981). Evaporation lagoon design often assumes minimization of flow throughout the design, construction and operating phases at a generating station. Experience has shown that often more wastewater is disposed of in the lagoon system than is allowed for in the design.

Care must be taken to ensure that evaporation rates are appropriate and conservative for the particular site chosen. Often, meteorological data for the site is not available, inappropriate measurements are used in design or the effect of the brine concentration is not considered for the evaporation rate. This has resulted in significant lagoon undersizing at several western U.S. generating stations. Pond liners are often selected without careful consideration of projected life, solids removal rate and expected brine chemistry. Additionally, seepage monitoring systems and provision for overflow

control are often not considered prior to lagoon constitution resulting in expensive retrofitting.

Lagoon evaporation systems are almost totally unforgiving and the slightest miscalculation or misunderstanding can lead to serious problems in the system operation (Rittenhouse, 1982). The impact of excess wastewater input to an evaporation lagoon can have significant economic impacts when additional lagoon capacity is necessitated. Based on 1982 cost estimates of lined lagoons of $40 000/ha(US) with an average annual evaporation rate of 1.2 L/ha, costs of $33 000(US) per additional litre per minute of brine to be evaporated are possible. These high costs, inflexibility and climatic dependence of evaporation lagoons now makes other brine disposal methods more attractive.

5.4.3 Salt Recovery. The feasibility of recovering sodium sulphate (Na_2SO_4) from wastewater brines by conventional evaporation and by interface enhanced vertical tube foam evaporation techniques has been investigated by Sephton (Sephton, 1976; 1980; Klein and Sephton, no date). The process shown in Figure 30 involves:

1) Ion exchange softening to remove calcium and magnesium to about 10 mg/L and replacing these with sodium ions exchanged from the resin.

2) Evaporation of the softening water by a cooling tower to permit a 5 to 20 times concentration. This required side stream treatment with aluminum sulphate and silica scale control.

3) Further 5 to 20 times concentration using vertical tube foam evaporation (VTFE) to achieve a salt concentration of 70 000 mg/L. This brine is used to regenerate the ion exchange resins in step 1 following clarification by foam flotation.

4) Evaporation - crystallization of the concentrated brine from the VTFE to produce sodium sulphate.

In addition to the possible commercial value of the removed sodium sulphate, the other economic advantage is the reduction in ultimate disposal costs by removing part of the Na_2SO_4 as a crystallized salt. The volume and final dissolved solids residue to be disposed of in the evaporation pond are reduced.

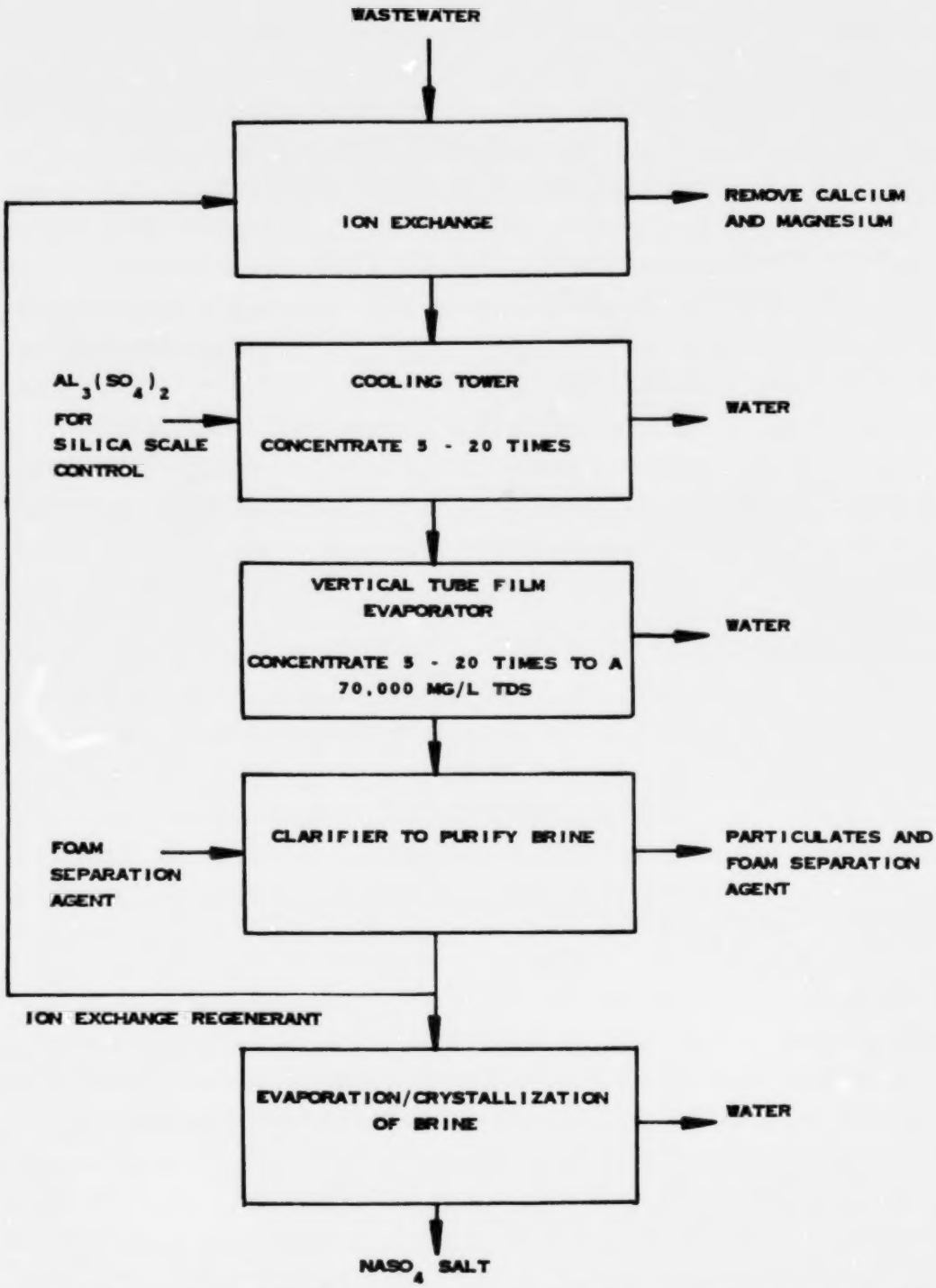


FIGURE 30 SODIUM SULPHATE SALT RECOVERY PROCESS (Sephton and Klein, 1976)

6 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

As with most other natural surface waters, Canadian surface waters vary somewhat from location to location with respect to TDS concentration and its compositional major and minor constituents. Species of aquatic organisms in these waters vary as well.

There appears to be general agreement that, in the absence of toxic element excess of essential element deficiency effects, osmotic pressure is a limiting factor for a variety of aquatic organisms. The safe range for this factor may vary from species to species, population to population and community to community. It may be influenced by the degree to which an organism has adapted or acclimated to a particular environment. Abrupt changes in natural TDS patterns which significantly affect osmotic pressure may have acute or chronic effects on communities or organism populations.

Most biological studies which have TDS/aquatic organism interactions have tended to be limited with regard to the degree and number of TDS compositional changes and organism considered. In a number of studies, either a more or less standard TDS composition, definition or detailed knowledge of the TDS constituents appears to have been assumed, since often the TDS definition, method used for TDS determination, and/or the major and minor constituents levels in the TDS under examination have not been reported. This presents significant result comparison difficulties and limits the conclusions which can be drawn with certainty.

There are a number of methods for the determination of TDS values. Significantly different 'TDS' values can be obtained by different methods when TDS constituents concentrations and composition ratios diverge from, or become 'abnormal' with respect to the concentrations and compositions encountered in most natural surface waters.

Industrial wastewaters may often be 'abnormal' with regard to major and minor TDS constituents. A number of the wastewaters which may arise during operation of coal-fuelled power generation stations for example, would be considered to have 'abnormal' TDS levels and compositions relative to natural surface waters. As a result, several of the methods commonly employed for the determination of TDS levels in natural surface waters may provide misleading TDS values if used for TDS determinations in these wastewaters. Since TDS composition may also vary considerably from stream to stream, the degree of inaccuracy may vary as well.

Few biological studies have examined the effects of 'abnormal' TDS composition on aquatic organisms and studies of the impacts of changes in naturally occurring dissolved solids on organisms are of limited use for judgement of the effects of industrial dissolved solids on environmental organisms. Consequently, it should not be assumed at present that overall industrial TDS levels which are comparable to those in adjacent natural waters are necessarily safe levels. Rather, until otherwise demonstrated, it should be assumed that they are potentially deleterious.

A number of methods for the reduction of TDS levels in industrial effluents are presently in use or under development. Some remove only certain of the major TDS constituents, others exchange one chemical species for another. Where 'abnormal' major ion ratios are produced, the potential long-term ecosystem effects resulting from discharge, are not well known yet. Rather than osmotic effects, specific major ion effects may be of more concern. However, with the development of new pollution control, water conservation and wastewater reduction system, TDS reduction technologies are becoming increasingly important. For some wastewater streams, TDS reduction technologies alone can improve wastewater quality sufficiently for system re-use or safe discharge. At the same time, better knowledge but the possible environmental effects of TDS discharges, significant major ion composition variations and synergistic effects in multi-component solutions will be increasingly required.

6.2 Conclusions and Recommendations

Some conclusions and recommendations which can be made based on the results of this study are:

- The average annual TDS concentrations in natural surface waters in Canada, with the exception of some of the arid prairies, are typically less than 300 mg/L. Constituents are primarily calcium, magnesium, sodium, bicarbonate, sulphate and chloride. This is in contrast to many industrial wastewaters which may contain higher TDS levels and have significantly different 'major' and 'minor' chemical species composition patterns. The development of an 'acceptable' TDS guideline which includes defined acceptable ranges for the major natural surface water TDS species, is desirable.

- Normal cyclic fluctuations in naturally occurring dissolved solids levels and their constituents seldom have drastic effects on the biology of freshwater systems. Since established organisms have adapted to such changes and the methods of

adaptation are diverse, it is unsafe to assume that abrupt man-induced (i.e., effluent discharge) alterations in these natural TDS patterns, would similarly produce little effect.

Since communities are composed of species populations and the methods of species adaptation to TDS patterns vary, the long-term effects of TDS changes on communities are difficult to judge on the basis of one or two short-term reactions to change by a species of a population. More long-term community response to TDS pattern alterations are required. However, in view of their complexity and time requirements, an interim recommended approach is to define 'acceptable' TDS levels in discharges very conservatively.

At least five methods of 'TDS' value determination have been developed. Each method has advantages and disadvantages for particular applications. Unfortunately, the values obtained by different methods may not be directly comparable. Consequently, the methods used for TDS determinations should always be stated when TDS results are presented. It would also be desirable to mention the particular limitations the procedure used.

- The evaporative method of TDS determination is widely used for the determination of TDS in industrial wastewaters. Although this method is subject to some ambiguity and error, it does not require prior assumptions to be made about the species composition or relationship between chemical species in the sample. Consequently, it is the recommended method for TDS determinations in industrial wastewaters when the complete TDS composition is not known or composition may vary significantly.

- Conductivity measurement of TDS in wastewaters should be limited to situations where the relationship to the evaporative method has been determined, anticipated. TDS compositional variations will not significantly affect this relationship and the possible error limits are acceptable.

- With the possible exception of filter washes and boiler room sump waters, all major wastewater streams in the coal-fuelled generating stations models in this study were indicated to contain total dissolved solids concentrations in excess of those normally found in the natural surface waters of Canada. In several cases TDS levels were several orders of magnitude greater than typical surface waters and in a number of instances the TDS constituents were 'abnormal' relative to natural water TDS

composition. When TDS levels approached normal surface water levels, the overall TDS value alone was not a reliable measure of the wastewater from an environmentally safe discharge perspective. In view of the present lack of information about the environmental safety of the discharge of 'abnormal' TDS content wastewaters, the development of conservative 'acceptable' discharge criteria for specific TDS reduction technologies discharges is recommended.

- Pretreatment of wastewaters is essential for the successful operation of most TDS reduction technologies. This is particularly true for wastewaters which are subject to fouling due to the precipitation of chemical species. The pretreatment requirements of TDS removal technologies should be included in the evaluation and comparative assessment of these technologies.

- TDS removal processes produce wastes in the form of highly concentrated brines or salt cakes. In some cases the economic recovery of salts may be possible. In all cases, these wastes must be managed and disposed of in an environmentally acceptable manner. This aspect should also be included in the evaluation and comparative assessment of TDS removal technologies.

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